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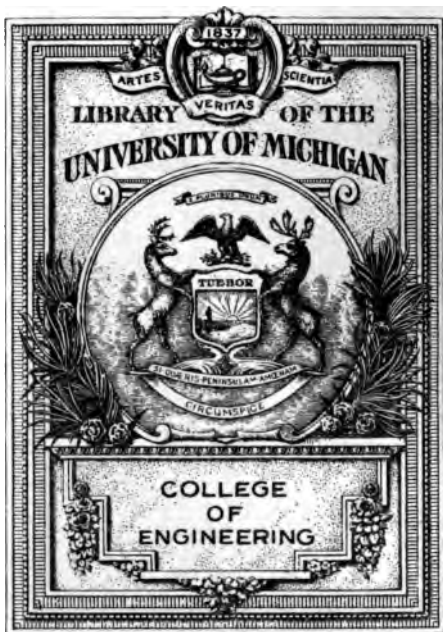
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GAS
ANALYSES
W·H·BIRCHMORE

BY N. G. G. G. G.



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THE INTERPRETATION OF GAS ANALYSES

EXPLICIT DIRECTIONS FOR
MAKING THE DEDUCTIONS NEEDED FOR UTILIZING THE
INFORMATION GIVEN BY A CHEMIST'S REPORT OF AN
ANALYSIS OF ILLUMINATING GAS, IN RESPECT
TO THE PROBLEMS DAILY DEMANDING
SOLUTION IN BUSINESS LIFE

BY
WOODBIDGE HALL BIRCHMORE, PH.D.



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To

THE FRIENDS WHOSE UNFAILING KINDNESS, GENEROUS
SYMPATHY AND STEADFAST ENCOURAGEMENT MADE
THIS BOOK POSSIBLE, IT IS DEDICATED AS
A TOKEN OF MY REGARD

407078

PREFACE.

The matter in the following pages makes no claims to originality, there is nothing in them which can not be deduced from statements in the classic works of Bunsen, Hempel and Winkler-Lunge, Dennis and probably still other writers — but it is the only book in which the implicit is made explicit. This is the reason for its being, that *it is the only book in which the directions for making the chemist's analysis a living thing, with the power to say something which the busy man can understand, is to be found in shape for instant use.* A satisfactory analysis can be made with apparatus costing less than five dollars, as the writer has demonstrated, and by following the directions of the book a deduction of the heating power of the gas, if by chance this is the item wanted, can be arrived at as accurately from the chemist's analysis as with any calorimeter costing half as many hundreds. The calorimeter can confirm, will confirm, the deductions from the results of the analysis as to the heating power of the gas, but it can do no more, it can never take the place of the analysis.

Many times men interested in gas-works have said to the writer “an analysis is useless to me, I would not know how to use it, and I could not make it mean anything.” To change this state of things has been the writer's hope, to put the gas-works-manager in such a situation that in a few minutes with a bit of

paper and a pencil he could answer any obvious question, or rather the three or four questions which conversations have seemed to show to be the obvious ones, has been the purpose in view.

If the instructions and suggestions given in the following pages shall prove equal to the task of showing "How to make a gas analysis useful" the writer's purpose will have been fully subserved.

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INTRODUCTION.

THIS small book is intended by its author to give an account of the methods employed for making a gas analysis *useful*, to give all the information essential for translating the memorandum given by the analyst into a form in which it will answer questions for which sufficient answers are demanded by the practical men, by the men who make the business of gas-making what it is, and who, although engaged in the greatest chemical industry of modern times, are usually by no means so familiar with special chemical calculations as they must sometimes wish to be.

The scope of this book. — It follows then that this book must begin just where the treatises on gas analysis and those on gas-making alike find the end of their subjects, in that it deals not with the methods of finding the various ingredients of the illuminating gas, (this is the business of the books on gas analysis, of the treatises of Hempel-Dennis and Winkler-Lunge), but with the methods of determining what an illuminating gas of a certain definite composition demands for its combustion, and what the results of this combustion will be, both chemically and physically, and in a sense mechanically.

The subjects with which this book is intended to deal find no place in the treatises, neither in the schemes of Hempel-Dennis nor of Winkler-Lunge. These books deal more or less exhaustively with the

methods and processes of finding the ingredients of an illuminating gas, but they tell but little and that little only by implication, never explicitly, of the propositions and deductions by which the lessons taught in their pages may be turned to practical account. These two just mentioned books to all intents and purposes represent the development of the art of analysis, they contain full specific and explicit directions for determining the ingredients of the mixtures which we call illuminating gas, in accordance with definite schemes, together with the amounts of the same in the mixture, and suggest the way in which the chemist having made the analysis shall report its results. These analyses may be made "in the works" by the chemist employed therein, they may be made perhaps by the manager himself, or they may be made by an analyst working in one of the many testing laboratories; in any case a blank will be filled out giving a statement per hundred or per thousand parts of the series of ingredients, which the author of the analytical scheme followed as a guide, has considered as the fundamental ingredient-series of this product of chemical industry. In other words, the analyst reports his findings, as he pursues his search, according to a definitely formulated plan, usually spoken of as the "analytical scheme." It is true that some other scheme may be used, but the chances are many to one that the routine employed will be either the Hempel-Dennis or the Winkler-Lunge scheme, and in this country we may be almost certain that it will be the routine of Hempel-Dennis.

These two schemes are not absolutely identical in plan, and they are both of them open to criticism, which has been very freely indulged in with respect to both of them, but the critics have offered nothing in their places, and no better methods seem likely to be devised. The differences between them however are just sufficient, while it remains a matter indifferent for the purposes of the gas works manager which one is considered the better by the analyst, to make it a matter of interest to know which one the analyst has used in any given case, for the results of two analyses of the same gas, one made by the Hempel system and the other by the Winkler plan, will be sure to differ just so much as is needed to cause endless confusion, if the facts in regard to the analyses and the systems used are unknown.

The differences in the systems. — As it is essential that those who use these pages “for working up an analysis” should know which system has been used it is best to give a résumé of the two methods and show how the respective items differ each from each. In order that the reader may be spared the inconvenience of a search they are given here.

The differences consist in part in the order in which the ingredients are sorted out, in part in the reagents used, and partly in the nomenclature. As the Hempel-Dennis system will probably be used the ingredients are given in the order of this system and its nomenclature is made the standard for the book.

1. “*Hydrocarbon vapors.*” — These are the ingredients absorbed by absolute alcohol, representing usually

vapors used for "enriching" the gas. This item is usually assumed to be equivalent to the third item in the system of Winkler-Lunge, and the component parts of it should be in theory at least benzene (benzol) C_6H_6 , and its isomeres and derivatives. In the Winkler-Lunge scheme they are assumed to be "burned up," oxidized that is, and converted into H_2O and CO_2 by "fuming nitric acid." It is by no means certain that these two items (1) Hempel and (3) Winkler are identical, nor is it certain that the ingredients taken out by these two reagents, a lcohol and fuming nitric acid, are the same in all gas samples.

2. "*Carbon dioxide.*" — In both systems this ingredient is absorbed by $NaOH$ or KOH . In the system of Winkler CO_2 is item 1.

3. "*Heavy hydrocarbons.*" — These are the ingredients belonging to the ethylene series. The system of Hempel-Dennis oxidizes them with anhydrous (fuming, Nordhausen) sulphuric acid, but the Winkler-Lunge system, in which they appear as item second, removes them with bromine.

4. "*Oxygen.*" — Like CO_2 an impurity. Estimated in various ways in both systems.

5. "*Carbon monoxide.*" — Sometimes absorbed, at others estimated by combustion.

6. "*Hydrogen.*" — Sometimes removed by fractional combustion "with palladium," but more frequently by "explosion" with oxygen. Usually this ingredient and the next are estimated in one operation, combustion with oxygen.

7. "*Light hydrocarbons,*" "*Marsh gas,*" "*Methane.*" — Sometimes this is reckoned as item 6, and the

hydrogen as 7. It is estimated indirectly by "explosion."

8. "*Nitrogen*." — This ingredient is estimated by difference and consequently contains the accumulated error of the analysis. It is well therefore to name this item "Nitrogen and Errors."

Owing to certain differences in results due to these differences in method the report of the composition of a given sample when examined by the system of Hempel-Dennis can not quite coincide in the statements of the amounts, except by accident, with the report of the composition of the same sample when examined by the method of Winkler-Lunge. The differences will be small but they will insist on being present. It follows therefore that when two reports of examinations made by different chemists present small differences, the first question to be asked is: "Did they use the same analytical system?"

For this reason, if for none other, the statement of the analytical system used should form part of the report. It would be an excellent thing if the manager of the works would insist on this statement of "system used" in every instance; the knowledge may on some occasion be of the utmost usefulness in many ways. In general one can distinguish the system which has been followed by the chemist in his analysis by taking notice of the order of the items in his report of his findings, and of the names used to indicate the ingredients which have been found. Sometimes the Hempel nomenclature is used in the Winkler order, then the position of the names may be a clue to the facts, but if an analysis is made by one system and

reported on blanks with the names and order of the other there is no clue to the facts. For these reasons a statement of the analytical system used in the examination should always be insisted on as part of the chemist's report.

The sample and its pedigree. — The record of the "pedigree" of a gas sample, which is always carefully recorded in the analytical chemist's office diary, if it be known by him, should also be made a matter of record in the gas works. It may be considered sufficient to mark the package with date and number when it is sent to the chemist, but in the works should be a record for the use of the manager giving the number of the specimen, the date (both day and hour) the particular fixture or "thief" from which the specimen was drawn, the pressure in the mains either in inches of water or millimeters of mercury, and last, but by no means least, the temperature of the gas in the mains and the temperature of the air at large and the height of the barometer.

The temperatures are important on account of the influence on the water contents of the gas, and the pressure and the barometer height are important as regulating the mass of the gas per meter cube. These items of the pedigree are essential; there are some others which seem to be desirable and even absolutely essential at times, but they are not demanded by every one in every case, as the writer, at least, thinks they should be.

The task of translation. — When the analyst has performed his task, when he has made his findings a

matter of record and this record has reached the works, then it is the task of some one to translate these data and to put them into a shape of use to the manager. To be an aid in this task, to make the work easy and accurate, the results certain and sufficient for all purposes, and full of meaning, is my little book's purpose. May it be of use in increasing human knowledge and in lightening human labor and my purpose will be attained.

One word as to its plan. — This book is worked in just the order and by just the system of reasoning I should use myself in each task which I have put before the reader and in each problem which I have discussed to solution.

The system and the distribution of the various items discussed is the result of nearly twenty-two years of study, during which two and twenty years my attention has been given in various situations to the chemistry of gases, illuminating gases in particular, as a science, and to the determination of the method best fitted for their employment as an art. During this period the work of analysis has been formulated and simplified by Winkler, Hempel and others until an intelligent boy can make a gas analysis as worthy of record, yes more worthy of record, than could Baron Bunsen himself but there has been wanting, and still is, unless this one proves to be satisfactory, *a single small book setting forth a system by which these findings by the analyst can be "worked up" to give the information the gas works manager needs and almost daily seeks to find in reference to the chemistry of the illuminating gas*

which he makes. The photometer will tell him the fact if his product is not up to standard in light-giving power, the calorimeter may tell him that the heating power is not up to standard, but the discussion of the chemical analysis and the study of the data thus obtained, and only these, can tell him *the reasons* for the facts of which the other two processes of investigation assure him.

Neither one of these methods of investigation and checking can take the place of the other two, the photometer will quickly make it plain if the luminosity falls off, but this is a consequence, not a reason; so also the calorimeter will say this gas is deficient in heat capacity, but only the chemical analysis can give the reasons why of both these unfortunate facts.

Therefore nothing can take the place of the chemical analysis and of the proper study of each return.

CHAPTER I.

THE TRANSLATION OF THE ANALYSIS.

WHEN the statement of the results of analysis is received from the analyst it is in a conventional form, and the gas is assumed to be in a condition never met with in practice. The gas is assumed to be water-free, the temperature to be 0° Centigrade scale, and the barometric pressure to be equal to that of a mercury column 760.0 mm. in height, conditions whose coincidence is so unlikely as to make the statement that they can never happen together in actual practice a perfectly safe one.

As the plan of this book is to show how to do everything discussed, exactly as if the work described were being done to get the information for use, it is needful to assume a gas sample and to discuss it in every way as if it were a sample studied in order that the information which the statement of the analyst contains may be brought into comprehensible form and be made useful for the guidance of the manager of the gas works. With this purpose in view I have chosen the sample of which the analysis is given in Hempel-Dennis. In that book the directions for making the analysis are given, and illustrated by an analysis; in this book the analysis therein given is discussed.

The reduction from conventional to actual conditions.

—The first business of the gas works manager, or

his deputy, under the circumstances named, is to put the data into such form that they will express the composition of the gas in the mains and at the burner; the composition of the damp, water-saturated gas at the actual temperature and pressure which are shown to have existed at the time when the gas was sent out by the recorded pedigree of the sample.

For the purposes of discussion we assume that the sample is found to have the same composition as that given in Hempel's "Gas Analysis," edited by Professor Dennis, edition of 1892, page 233.

COMPOSITION OF THE GAS SAMPLE. (TABLE I.)

Gas dry. Temp. 0° C. Barometer 760.0 mm. Date May 8, 1892.

Hydrocarbon vapors.....	0.6 per cent.
Carbon dioxide	3.4 " "
Heavy hydrocarbons.....	4.4 " "
Oxygen.....	0.3 " "
Carbon monoxide	10.1 " "
Marsh gas.....	30.6 " "
Hydrogen.....	45.9 " "
Nitrogen and loss	4.7 " "
	<hr/> 100.0

It will be noted that this statement is really in parts per thousand, this being the number of parts into which the Hempel burette is divided. Why this result is expressed in the form of tenths per cent. instead of in the more sensible one of cubic centimeters per liter, or of liters per cubic meter, which are equally parts per thousand, is not evident. The above statement may be read as parts per thousand by omitting the decimal point, and it is in many ways better in copying into the diary of the works to omit the point

and to copy as liters per cubic meter. This form of report, the one expressed in parts per thousand, is the only one which should be made for commercial purposes; it makes not the slightest difference whose burette is used, in practice the size is limited to 100 c.c. and the smallest possible reading is one tenth cubic centimeter—again one per thousand. When the so-called “exact method” is used, when not the bulk of the gas but its tension is measured, a much finer reading is possible, but it is inconsistent with the probabilities to assume that “the exact method” would be used in the examination of a gas sample under the conditions imposed, and this because the technic of exact examinations takes too much time to make them profitable. While one part per thousand is the practical limit in examination by Hempel’s so-called technical method, in examinations by the exact method a statement in terms of one part per hundred thousand is by no means improbable, since with a cathometer a reading to the one hundredth millimeter or even finer may be attained, although the one hundredth millimeter seems to be the practical limit. With this class of analyses we have in this book nothing to do, the analyses we are to discuss here are of the kind called “technical” by Hempel, in which analyses the confining fluid is water.

The correction for temperature and pressure and the change from “dry gas” to “moist gas,” or in the reverse direction.—The first correction which must be considered after the analysis has been made a matter of record is the correction for moisture, for tempera-

ture and for pressure. In order that these corrections may be used the temperature and the barometric height must be known; for this reason the necessity of having these two instruments, the barometer and thermometer, in daily use—yes, in true hourly use—is insisted on.

The barometer.—The most satisfactory barometer for use in a gas works laboratory, or in a counting room for the sake of the record, is that one which can be read by the average employee with the least probability of mistake. This at once eliminates the complicated patterns used by the weather bureau. It also eliminates the common aneroids, which are almost never read correctly and practically limits us to the form known as “Bunsen’s with sliding-scale.” This particular pattern has two advantages: it is inexpensive, in fact it is the cheapest good one made, and it can be read accurately and with speed, and that to the smallest rational limit, one half millimeter, by any one who can read a barometer at all. In the short arm of this instrument stands a thermometer by which the temperature of the mercury is determined. Care should be taken to hang the barometer in a situation which will insure its being either at the temperature of the outside air or at that of the room, not against an outside wall—in which case its temperature is neither outside nor inside—or against the partition between a warm room and a cold one. In making record of the barometer reading the reading of this thermometer should also be noted in brackets, thus, Bar. 758.2 (18.4° C.), and the time of day when the reading is

made should be recorded accurately. The importance of knowing the pressure of the atmosphere is very great and many an exasperating, nerve-destroying puzzle disappears if this factor is but known.

The graduation of the barometer.—This must be left to individual taste. Some persons make use of a barometer graduated to inches. This was for a long time the only graduation used in England and America; hence such barometers are often spoken of as “English barometers,” no matter where they are made, and once in a while the terms “English graduation” and “French graduation” are used for the inch and millimeter graduations respectively.

The standard barometric height for the “English graduation” is (30”) thirty inches, and that for the “French graduation” is 0.76 meter (760.0 mm.). By this nomenclature is expressed the fact that the pressure of the atmosphere against a perfect vacuum will sustain a column of mercury thirty inches (30”) or seven hundred and sixty millimeters (760.0 mm.) high. This assumption is the cause of trouble at once; “one atmosphere,” pressure English, is not quite the same thing as “one atmosphere” pressure metric. The 760.0 mm. actually equals 29.9215 ins. not 30 ins., and one atmosphere English equals 243.054 avd. ounces, as against one atmosphere metric at 242.418 ounces. In pounds these weights are 15.1909 lbs. and 15.1512 lbs., consequently the difference is almost one twenty-fifth of one pound; exactly 0.0397 lb. or 0.636 oz.

This difference is small, but it should be taken into account when converting the quantities of one system

into quantities of the other system. If only a rough approximation is wanted the barometric height in inches may be changed to millimeters, and the reverse by using the factor 25.4, that is, inches \times 25.4 = millimeters and millimeters \div 25.4 = inches. If more accurate approximation is desired it is better to use the logarithmic factors throughout, but such calculations are a waste of time. The proper method is to use a barometer graduated to the metric units.

The thermometers. — As has been said the reading of the thermometer in the short arm of the barometer tube must be given not as an evidence of the temperature of the gas in the mains, but for the purpose of reducing the expression of the barometric height to 0° C. should this for any reason become advantageous. The temperature of the gas in the main, or in the holder, as the case may be, should be taken by means of a thermometer actually in contact with it, and if this contact can be established both in main and holder so much the better, but in any event pains must be taken to see that the reading is the temperature of the gas in the mains, and not that of the atmosphere nor of some building. If it is inconvenient to take the temperature in the mains the temperature in the gas holder may be taken, but I have often seen the temperature in the holder seven or even ten centigrades above the temperature in the mains, and this stands for water in the pipes to a dead certainty. The word "centigrade" is often used for "degree centigrade" and the expression "ten centigrades" (written 10° C.) is exactly the same as "ten degrees centigrade thermometer," and it saves time and space.

Unfortunately the centigrade thermometer is less frequently used than the so-called Fahrenheit thermometer which has a different graduation and another zero point. The conversion of one scale into the other is simple enough :

$$\text{Temp. Centigrade} = \frac{5}{9} \times (\text{temp. Fahrenheit} - 32^{\circ}).$$

$$\text{Temp. Fahrenheit} = \left(\frac{9}{5} \times \text{temp. Centigrade}\right) + 32^{\circ}.$$

In addition to these two scales are the two shapes of the so-called "absolute scale," which, used in an immense number of calculations, are practically without instrumental expression.

These so-called absolute scales are in use as developments, the one of the Centigrade scale, the other of the Fahrenheit. To convert a given temperature Centigrade into its corresponding temperature by the absolute scale, that is to obtain the absolute temperature reading, we add to the reading 273, in other words the temperature $18.4^{\circ} \text{C.} = 291.4^{\circ} \text{A.}$ The conversion of the Fahrenheit scale is not so easy, but in practice a limited use is found of an arbitrary equivalent obtained from the equation given previously and the "absolute zero" is considered to be -459.4°F. , and if there were an absolute Fahrenheit scale its readings would be found by adding 459.4 to the Fahrenheit reading; hence 60°F. would be equal to 519.4 absolute scale, Fahrenheit reading. In this way we obtain for the "boiling point" of water 212°F. , 100°C. , 373°A. and 671.4°A. Fahrenheit reading. We can now consider the version of the report as it reads in the records of the works; in the office of the manager,

that is in the "Manager's Journal," or in the "Chemist's Journal" in the laboratory of the works, if "the works" maintains this adjunct.

To complete the record a temperature and barometric pressure must be assumed since they are important items in the data of the discussion. We assume the thermometer reading to be 16°C . and that the barometric pressure is 758.2 mm.

TABLE II. THE MANAGER'S RECORD.

Date, May 8, 1892. Specimen taken at 10:30 a. m. from fixture 7a.

Barometer 758.2 ($16^{\circ}\text{C}.$).

Temperature of atmosphere $16^{\circ}\text{C}.$ Tension of water vapor 12.6739 mm.

Temperature in mains $12.0^{\circ}\text{C}.$

Pressure at fixture 7a = 2.58 water inches.

Chemist's report temp. $0^{\circ}\text{C}.$ Bar. 760.0 mm.

			Liters @ *
			Meter Cube.
1. Watery vapor.....		H_2O	14.3
2. Hydrocarbon vapors.....	0.6 per cent.	C_6H_6	5.9
3. Carbon dioxide.....	3.4 " "	CO_2	33.5
4. Heavy hydrocarbons.....	4.4 " "	C_2H_4	43.4
5. Oxygen.....	0.3 " "	O_2	3.0
6. Carbon monoxide	10.1 " "	CO	99.6
7. Hydrogen.....	45.9 " "	H_2	452.4
8. Marsh gas	30.6 " "	CH_4	301.6
9. Nitrogen, and loss.....	4.7 " "	N_2	46.3
			1,000.0

From the data given in this report it follows that some one has taken the trouble to convert these percentages of dry gas composition data at $0^{\circ}\text{C}.$ and 760.0 mm. into terms of the saturated gas at the observed temperature and pressure. Since the reader

* Above is figured from temperature *in the main*, since this controls its H_2O content when issuing from the burner.

will need to do this thing and will best do it in the same way the method used is explained here. It must be remembered that as long as the gas is conceived as dry the proportions (percentages) by volume of the various ingredients will not change with temperature and pressure no matter how much the mass may change, but once the vapor of water is introduced into the gas changes in percentage composition due to change in temperature will begin.

The formulæ used for reduction.—The two formulæ which are used in determining the values under the changing conditions are

$$V^o = V^t \times \frac{273}{(273 + t)} \times \frac{(B - f)}{760}$$

and the converse proposition

$$V^t = V^o \times \frac{(273 + t)}{273} \times \frac{760}{(B - f)}$$

The first of these has, it may be, been already used by the chemist for reducing his data, obtained by experiment, from the actual to the conventional conditions. In these formulæ V^o = volume of gas at 0 C.°, V^t = volume at some temperature t° . B = the barometric pressure and f is the value for the elastic force of watery vapor at the temperature t° , which value, f , must be obtained from a table giving the tension of watery vapor. Such a table is given at the end of this book.

In the process of making a chemical analysis useful it may be needful to discuss its data as true at various

temperatures, and it may be needful to consider the water content as variously distributed. Considering first the situation at 0 C.° and 760 mm.:

Under these conditions

$$V' = V^o \times \frac{273 + 0}{273} \times \frac{760}{760 - f},$$

and we find from the table referred to that $f = 4.5687$ mm. of mercury, say 4.6. Hence

$$V' = V^o \times \frac{273}{273} \times \frac{760}{755.4} = 1.0065 \times V^o.$$

If then we multiply the given bulk of each ingredient by this factor, we indicate its volume when increased by the amount of water dissolved in it; in other words the bulk of the water-saturated gas at zero, as compared with the dry gas at the same temperature and the same pressure. If we wish to transform the various items to the bulk which they would occupy under the conditions of temperature and pressure which are stated to have been those of the gas at the fixture, that is at the temperature and under the pressure of the atmosphere, then the formula takes the shape

$$V' = V^o \times \frac{273 + 12.6}{273} \times \frac{760}{758.2 - 10.85} = 1.06387.*$$

$$* V' = V^o \times \frac{273 + 12.6}{273} \times \frac{760}{758.2 - 10.85}$$

$$= V^o \times \frac{285.6}{273} \times \frac{760}{747.35}$$

$$V' = V^o \times 1.06387$$

$$\text{Log } 285.6 = 2.4557582$$

$$\text{Log } 760.0 = 2.8808136$$

$$\text{a. c. Log } 273.0 = 7.5638374 - 10$$

$$\text{a. c. Log } 747.35 = 7.1264760 - 10$$

$$\text{Log num. portion} = 0.0268852$$

$$= \text{Log } 1.06387$$

The quantity t° or 12.6 C.° is the temperature as previously stated and 758.2 is the barometric height, while 10.85 is the tabular value of f . Performing the operations indicated, the numerical portion of the above equation reduces to 1.06 and $V' = V^{\circ} \times 1.064$. As before, if we multiply each item by 1.064 , we obtain a representation of its bulk at the desired temperature when water-saturated, and the summation is found to equal 1.064 per cent. of the value of the dry gas. It is obvious under these circumstances that the proportions of the various items in a liter might retain the same value, but the amount of the useful ingredients in a given bulk would have been reduced to a certain extent. In order that this may be made appreciable and distinct, it is a wise plan to assemble the watery vapor as an item and evaluate it.

The watery vapor considered as a special item.—The tension of the water vapor in any volume of gas is primarily dependent upon the temperature, but the pressure of the atmosphere determines its apparent bulk. Taking up the quantities at 0 C.° and 760 mm. we find the "tension" given in the table; it is 4.5687 mm. That is to say, the elastic force of the watery vapor is equal to the pressure of a column of mercury 4.5687 mm. high when such vapor is expanded to unit bulk at 0 C.° .

It follows thence that its volume at 760 mm. will be, since it is proportional to the pressure,

$\frac{760}{4.5687}$
 $= 166.34$
 $\times 1.064$
 $= 176.4$

$$\frac{100 \times 4.5687}{760} = 0.601145 \text{ c.c. in } 100,^*$$

or 6.01145 c.c. per liter. Since this is the bulk of the H_2O vapor considered as a single item the remaining ingredients will fill the volume of $1.000 - 6.01145 = 993.98855$, or omitting the last three decimal figures, = 993.99 or 993.989 for greater accuracy.

If we multiply the percentage column of the table item by item by this factor we would obtain the relative bulk of the ingredients in the H_2O -saturated gas when the thermometer is 0°C. and the barometer 760.0 mm.

The tension in millimeters of mercury answering to the temperature 12.6°C. is 10.8503 mm. This, when the barometer is 760.0 mm., is represented by 14.2767† liters @ cubic meter, but since in the case in hand the barometer is not at 760.0 mm., but is at 758.2 mm., the bulk of the H_2O vapor will be increased to

$$14.277 \times \frac{760}{758.2} = 14.3106 \text{ liters,}^\ddagger$$

* The proportion is $760 : 4.5687 :: 100 : \phi$

$$\begin{array}{rcl} \text{Log } 100 & = & 2.0000000 \\ \text{Log } 4.5687 & = & 0.6597926 \\ \text{a. c. Log } 760 & = & 7.1191864 - 10 \\ & & 9.7789790 - 10 = \text{Log } 0.601145. \end{array}$$

† $760 : 10.8503 :: 1000 : \phi$

$$\begin{array}{rcl} \text{Log } 10.8503 & = & 1.03544173 \\ \text{Log } 1000.0 & = & 3.0000000 \\ \text{a. c. Log } 760 & = & 7.1191864 - 10 \\ & & 1.15462813 = \text{Log } 14.2767. \end{array}$$

‡ The proportion is $758.2 : 760 :: 14.2767 : \phi$

$$\begin{array}{rcl} \text{Log } 14.2767 & = & 1.15462813 \\ \text{Log } 760 & = & 2.8808136 \\ \text{a. c. Log } 758.2 & = & 7.1202162 - 10 \\ & & 1.15565793 = \text{Log } 14.3106. \end{array}$$

or 14.3 liters, the value given in the table. The values of the remaining items may be, from this known value, calculated in the way just now suggested— $1000 - 14.3 = 985.7$ and $n \times 985.7 = m$ the value given in the table.

The formulæ

$$V^o = V^n \times \frac{(B-f)}{760} \times \frac{273}{273+t}$$

and

$$V^n = V^o \times \frac{760}{B-f} \times \frac{273+t}{273}.$$

As these two formulæ, or their components, are required for use each time one wishes to construct an equation in reference to gas physics it is as well to consider them by themselves.

Each of them is divisible into two primary ones; one deals with the results of temperature changes, the other with the results of changes in the atmosphere's density or weight. The forms in which they are used may be considered at length.

Case 1. — Given the volume of a gas at some temperature, n C.°, what volume will it occupy at some other temperature m C.°, the barometric height not changing? Assume the volumes to be represented by V^n and V^m , then since gas volumes vary directly as the temperature we write

$$T^n : V^n :: T^m : V^m;$$

if V^m is the unknown we may write

$$V^m = V^n \frac{T^m}{T^n}.$$

From this we infer—

Case 2. — Given the temperature of one of two volumes of gas to determine the temperature of the other the barometric pressure being constant. From case 1 we have

$$V^m = V^n \times \frac{T^m}{T^n},$$

hence

$$T^m = T^n \frac{V^m}{V^n}.$$

These temperatures are reckoned on the absolute scale and to obtain them 273 must be added to the Centigrade reading.

As illustrative examples. *Case 1.* What space will the air occupy at 18 C.° which fills 150 cubic feet at 15 C.°?

$$T^m : V^m :: T^n : V^n,$$

or in figures

$$288 : 150 :: 291 : X,$$

or

$$X = \frac{150 \times 291}{288}, \text{ or } = 151.57 \text{ cubic feet.}$$

Case 2 may be illustrated by reversing the terms of the above. At 18 C.° a volume of air fills 151.57 cu. ft.; at what temperature will it fill 150 cu. ft.?

$$V^m : T^m :: V^n : T^n,$$

or in the figures

$$151.57 : 18 :: 150 : X,$$

or

$$X = \frac{150 \times 18}{151.57}, \text{ or } = 15 \text{ C.}^\circ.$$

Case 3. — Since gases expand with a rise of temperature they, or rather their volumes, are said to vary directly with the temperature, but this is not the case with regard to the pressure, for the volumes of gases increase as the barometric pressure falls, and therefore they vary inversely. In the above examples

$$V^m : T^m :: V^n : T^n$$

or

$$V^m = T^m \times \frac{V^n}{T^n} \text{ and } \frac{V^m}{T^m} = \frac{V^n}{T^n};$$

but if the pressures are considered,

$$V^m : V^n :: P^n : P^m,$$

hence

$$V^m \times P^m = V^n \times P^n \text{ and } V^m = \frac{V^n \times P^n}{P^m}.$$

To illustrate this "What space will that volume of air occupy when the barometer stands at 734.0 mm. which occupies 421 c.c. when the barometer stands at 755.0 mm. ?

$$V^m : V^n :: P^n : P^m,$$

hence

$$V^m = \frac{421 \times 755}{734} = 434.41.$$

Case 4 is the reciprocal of this one. Given the space which a volume of air occupies under a given pressure, under what pressure will it occupy another given space, larger or smaller? The proportion and equation may be written,

$$P^m : P^n :: V^n : V^m$$

and

$$P^m = \frac{P^n \times V^n}{V^m}.$$

Using the numerical quantities above,

$$P^m = \frac{421 \times 755}{434.41} = 734 \text{ mm.}$$

Case 5 combines both these, and the equation may be written

$$V^m = V^n \times \frac{T^m}{T^n} \times \frac{P^n}{P^m}.$$

If we assume V^n to be the volume at 0 C.° and 760 mm. and V^m the volume at 10 C.° and 759 mm. we would write

$$V^m = V^n \times \frac{273 + 10}{273} \times \frac{760}{759},$$

that is the volume V^m increases for both causes as we know it should—from temperature because the thermometer has risen, the gas is warmer and expands; the barometer has fallen, from this cause also the volume increases.

Case 6.—Hitherto we have been considering dry gases only, but if the gas be water-saturated a new factor is introduced. This factor, f , the tension of the watery vapor, is a function of the temperature, but as it is measured in millimeters of mercury pressure it is treated in practice as a function of P , and this last equation takes the form

$$V^m = V^n \times \frac{T^m}{T^n} \times \frac{P^n}{P^m - f}.$$

At the temperature + 10 C.° the value of f is 9.1398 mm., hence using the same numerical quantities as before

$$V^m = V^n \times \frac{273 + 10}{273} \times \frac{760}{759 - 9.1398};$$

if for V^n we write V^o and for P^n , 760. This last may be written

$$V^n = V^o \times \frac{273 + t}{273} \times \frac{760}{B - f};$$

hence

$$V^o = V^n \times \frac{273}{273 + t} \times \frac{B - f}{760},$$

which is the form in which these formulæ usually appear in practice.

It often happens for the sake of precision that some other shape is more convenient, hence the changes are given in full.

CHAPTER II.

THE ATMOSPHERE. SPECIFIC GRAVITIES AND LITER WEIGHTS.

AFTER the fuel the great factor in all combustion processes is the air, the gaseous ocean which surrounds the whole earth and at the bottom of which we may be said to live, move and have our being, since without the atmosphere, this air-ocean, or more properly its active constituent oxygen, O_2 , all combustion, and all life, so far as we know either combustion or life, would be impossible.

In regard to this air-ocean a number of facts must be considered by the manufacturer of illuminating gas. Differences in the mass weight over limited areas, which often occur in the atmosphere from time to time, determine changes in the mass of a given bulk of gas, and therefore also determine how much gas, expressed in terms of weight units, must be reckoned to the cubic foot—or meter. Differences in the temperature of the air-ocean determine how much watery vapor both air and gas shall carry, which amount of watery vapor is to the gas works manager the cause of ever-present fear, of frequent trouble and great loss, and sometimes for most unlooked-for gain.

The weight of the unit bulk.—By the weight of the unit volume the chemist determines the specific gravity of any gas, comparing the weight of the unit

volume, be it a liter or a cubic meter, of the gas under consideration with that of the same volume of air. On this account it is of the utmost importance that the weight of the atmosphere shall be accurately known. Unfortunately there is nothing in connection with the whole question of gas making less certain than the relative weights of equal bulks of illuminating gas and air, unless it be the weight of a unit bulk of air and its chemical composition if temperature, pressure, humidity, etc., are not taken into account and a complicated calculation made. Many chemists have studied the composition of the air and many physicists its weight; but while their results are surprisingly in concord, and while these said results unquestionably show the same composition throughout the whole earth under like relative conditions, this agreement, which is so marked a characteristic of the results obtained from a study of the chemists' work, is wanting to the chemists' words. The published findings of the chemists do not by any means express a uniform conclusion, on their part, as to the composition of the air because the exact condition of observations are not in many cases stated.

Nor do the physicists agree any better in their determinations of the liter weights of the individual gases and vapors and their determinations of the relations between these weights and those of dry air show no less a want of uniformity. Hence in dealing with the problems discussed in this chapter it is absolutely needful to have a clear understanding of the way, or ways, in which our present conceptions of our own

results, or findings, are influenced by, or in their turn influence, our understanding of the past acts of others.

One word of caution is in order here. To those not familiar with the subject a table of specific gravities and liter weights is always a table of specific gravities and liter weights, and those who are in haste often accept any quantity given in a list as one having the right to be recognized for a true statement of relation without asking who vouches for the accuracy of determination and correct quotation of the findings, item by item — and this should not so be. There are tables which represent actual determinations and carefully made calculations, and these when properly used bring out results reasonably near to accuracy, or at least to agreement, but there are others which are simply compilations copied from hither and from yon without the least regard to authority or propriety, and since these are the most numerous they are also the most easily available ; they are therefore the ones, the very ones, most frequently made use of, and that by those with whose reputation heedlessness of any nature seems to be utterly incompatible.

Among the multitude of lists there are three series of determinations which rest on very careful work, the determinations by Bunsen, by Hempel and by Von Jolly. But these are not to be accounted equally reliable in all respects. Bunsen's determinations were made with reference to a special place, his laboratory in Berlin, and in his great book on gas analysis he is careful to thus specify, saying that they hold good for a thermometer at 0 C.°, a barometer height of 760.0

mm. at his laboratory at Berlin, latitude $52^{\circ} 31' 13''$, and at an elevation above sea-level of 41 meters.

Hempel in his book gives two determinations,* one for the same place and condition as Bunsen's and one for the sea-level at latitude 45° . Von Jolly has made determinations of weights and specific gravities assuming a thermometer of 0°C. and a barometer of 760.0 mm. but does not give the latitude nor height above sea-level.

To anyone who has given the question anxious attention it must be apparent that the series which can most properly be used by the "gas manager" are the second series of Hempel, those for latitude 45° and the sea-level, or rather they would be did they in all points agree with themselves which they do not, still they are the best and most useful within reach.

If the American Gas Light Association would promulgate a resolution declaring the series of values published by the Smithsonian Institution with the imprimatur of Langley was the one to be hereafter used in all calculations in which its members were interested they would do well; if they would extend this action and declare that not 760.0 mm. but 1,000 mm. was hereafter to be their standard barometer and have the table refigured for the mean radius of the osculating spheroid at Lat. 45° as recently determined by the Coast Survey and have the series printed in their transactions, they would do still better.

The composition of the air. — The chemist has to consider the composition and weight of the air in a number of different ways, and every one of these more

* Quoted from Landolt and Bernstein.

or less, much more rather than less, concern the gas works manager. Both alike have to deal with this gas mixture, the atmosphere, when dry and when saturated with water, which makes a division into two phases and in each phase are a number of problems which may be tabled. The purpose in discussing them is to impress upon the minds of all who may use this book the necessity of some standard value of γ and of the like weights if we are ever to escape from the present confusion of the data.

A. *The air being dry.*—The gas manager may need to know :

1. The composition of a thousand parts by volume, *i. e.*, in terms of cubic centimeters per liter, or liters per cubic meter, temperature and pressure normal.

2. The composition by weight of a thousand parts by volume = grammes of O_2 and N_2 in one liter of dry air at 0 C.° and 760.0 mm. barometric pressure.

3. The composition by volume of a thousand parts by weight = cubic centimeters of O_2 and N_2 in one kilogramme of dry air at 0 C.° and 760.0 mm barometric pressure.

4. The composition of one thousand parts by weight.

5. The conditions of composition under the arbitrary values of normal situation, temperature and pressure.

B. *The air being water-saturated.*—The above five questions must be answered under this division as equally important.

1. The first item to be discussed and, if possible, to be determined is this one, "*What is the composition by volume of a cubic meter of waterless air at 0 C.° and 760.0 mm. barometer?*"

As the mean of twenty-seven determinations given by Bunsen ("Methoden," 1877),

$$\text{O}_2 = 209.3 \text{ liters per meter cube,}$$

$$\text{N}_2 = 790.7 \quad " \quad " \quad " \quad "$$

but, as for the table on page 383 of the said book, his final opinion is that the composition is best expressed by $\text{O}_2 = 209.6$ and $\text{N}_2 = 790.4$. He nowhere gives his reason for the difference in statements. Von Jolly, as given by Winkler-Lunge, found the composition to be under the same conditions of temperature and pressure $\text{O}_2 = 207.45$ liters per meter-cube and $\text{N}_2 = 792.55$, a decidedly important difference. *

In his book on gas analysis Hempel nowhere gives his view of the volumetric composition of air, but from various inferences he seems to regard the average composition as not far from $\text{O}_2 = 209.5$ and $\text{N}_2 = 790.5$ liters per meter cube, which figures are near to being Bunsen's, but this composition will not reconcile with his dicta in relation to the liter weights.

TABLE A. COMPOSITION OF THEORETICAL ATMOSPHERE BY VOLUME.

Authority.	At.	O ₂ .	N ₂ .	
Bunsen	Berlin	209.30	790.70	Mean of 27 determinations.
Bunsen	Berlin	209.60	790.40	Bunsen's assumed values.
Von Jolly	Not stated	207.45	792.55	
Hempel	Berlin	209.50	790.50	Mean of Oertel's determinations.

2. "What is the composition by weight (grammes) of one meter cube of atmospheric air, water-free, under conventional conditions?"

Hempel gives two values for the weights per liter, one at the sea-level in latitude 45°, the other at Ber-

* The air undoubtedly differs slightly in composition at different places.

lin; the first of these he gives as 1,293.052 grammes per meter cube and the second as 1,293.909 grammes.

This difference in weight, 0.857 grammes, is due to the fact that a pressure corresponding to the normal barometer, 760.0 mm., at Berlin will be much greater than that corresponding to the normal barometer at the sea-level and at the latitude 45° . It is for this reason that it is so very desirable to introduce the limitation of place into our discussions. The differing-values of γ due to geographical situation make the notion that a reduction to C. $^{\circ}$ zero and 760.0 is a finality a most mistaken one. As matters now stand we can not compare the relations of determinations made at different places unless we know the value of γ in all of them, and allow for it. Usually it is difficult to obtain the information for this correction and often it is impossible.

Winkler and Lunge give the weight of a liter of air "in the normal state" as 1.2922 grammes. A cubic meter therefore weighs 1292.2 grammes, *but where? Not everywhere*, that is certain.

Bunsen gives the weight per cubic meter at Berlin as 1,293.6 grammes per meter cube, and gives the latitude of Berlin as $52^{\circ} 31' 13''$ and its elevation as 41 meters. This introduction of these quantities, even incidentally, shows that he understood their importance.

From these figures it appears that one can find authority for stating the composition by weight of air per 1,000 parts by volume in very diverse terms. He may give it as 299.3923 grammes oxygen and 991.6032 grammes nitrogen, as being the result from

Hempel's figures for lat. 45° and sea-level with standard temperature and pressure, or as 299.7905 grammes oxygen and 993.2168 grammes nitrogen, quoting Bunsen's values, the conditions being the same, but the location Berlin.

TABLE B. SHOWING DISCREPANCIES IN THE COMMONLY USED STANDARDS IN RELATION TO WEIGHT AND COMPOSITION OF THE ATMOSPHERE.*

1 Author.	2 Location	3 Weight of Air @ Meter Cube.	4 Liters of O ₂ in Meter Cube.	5 Weight of O ₂ Grammes.	6 Liters of N ₂ in Meter Cube.	7 Weight of N ₂ Grammes.	8 Sum of No. 5 and No. 7.
Bunsen.	Berlin.	1293.60	209.60	299.7905	790.40	993.2168	1293.0073
Hempel.	Berlin.	1293.909	209.50	299.5913	790.50	992.2593	1291.8506
Hempel.	Lat. 45° S. L.	1293.052	209.50	299.3923	790.50	991.6032	1290.9955
Jolly.	Not stated.	1292.20	207.45	296.6534	792.55	995.6014	1292.7548

The figures given as Jolly's are taken from Lunge's Winkler.

The density of *atmospheric* nitrogen according to Rayleigh is 0.97209 and the weight of one liter 1.25718 grams. If these figures are used in the calculations,

* Data of above calculation :

Author.	Liters of O ₂ .	Log.	Weight of O ₂ @ Liter.	Log Weight O ₂ .	Log of Product.	Product.
Bunsen.	209.6	2.3213913	1.4303	0.1554271	2.4768184	299.7905
Hempel.	209.5	2.3211840	1.43003	0.15534515	2.47652915	299.5913
Hempel.	209.5	2.3211840	1.42908	0.15505652	2.47624052	299.3923
Jolly.	207.45	2.3169134	1.43000	0.1553360	2.4722494	296.6534

Author.	Liters of N ₂ .	Log.	Weight of N ₂ @ Liter.	Log Weight N ₂ .			Sum.
Bunsen.	799.4	2.8978469	1.2566	0.0991971	2.9970440	993.2168	1293.0073
Hempel.	790.5	2.8979019	1.25523	0.09872328	2.99662518	992.2593	1291.8506
Hempel.	790.5	2.8979019	1.2544	0.0984360	2.9963379	991.6032	1290.9954
Jolly.	792.55	2.8990267	1.2562	0.0990588	2.9980855	995.6014	1292.2548

instead of the density of *pure* nitrogen, the sum of the parts will be much nearer the whole, at least for Hempel's values, which are probably the most accurate.

3. *The composition by volume of 1,000 parts by weight.*

If we accept Bunsen's result and say that a cubic meter contains 1,293.6 grammes of air under normal conditions 1,000 grammes will fill 773.04^1 cubic centimeters, which will contain, says Bunsen, 162.029^2 O_2 and 611.011^3 N_2 , while Hempel's figures (1,293.052 gm.) give 162.02^5 O_2 and 611.3443^6 c.c. N_2 , 773.3642^4 and Jolly's (1,292.2) give 160.54^8 c.c. O_2 with 613.334^9 c.c. $N_2 = 773.8742^7$ differences bizarre and confusing enough, *unless we know the locations of these observations.**

* 1. The proportion is $1293.6 : 1000 :: 1000 : \phi$

$$\text{Log } 1000 = 3.000000$$

$$\text{Log } 1000 = 3.000000$$

$$\text{a. c. Log } 1293.6 = 6.8882000 - 10$$

$$\hline 2.8882000 = \text{Log } 773.04$$

2. $1000 : 209.6 :: 773.04 : 162.029$

3. $1000 : 790.4 :: 773.04 : 611.011$

4. $\text{Log } 1000^1 = 6.0000000$

$$\text{a. c. Log } 1293.052 = 6.888384028 - 10$$

$$\hline 2.888384028 = \text{Log } 773.3642$$

5. $1000 : 209.5 :: 773.3642 : \phi$

$$\text{Log } 773.3642 = 2.888384028$$

$$\text{Log } 209.5 = 2.3211840$$

$$\text{a. c. Log } 1000 = 7 - 10$$

$$\hline 2.209568028 = \text{Log } 162.02$$

6. $1000 : 790.5 :: 773.3642 : \phi$

$$\text{Log } 773.3642 = 2.888384028$$

$$\text{a. c. Log } 1000 = 7 - 10$$

$$\text{Log } 790.5 = 2.8979019$$

$$\hline 2.786285928 = \text{Log } 611.3443$$

4. *The composition of 1,000 parts by weight.*

The fact that the liter weights of oxygen and nitrogen are not in the same proportion as their space ratio in the air gives to the air a composition @ 1,000 parts by weight other than the composition @ 1,000 parts by volume. Making use of the values in Table B we obtain the values in Table C, but the same lack of agreement appears, and we find 231.4587 grammes of oxygen and 768.5413 grammes of nitrogen, if Hempel's data are used, and 231.8493 grammes oxygen and 768.1507 grammes nitrogen if we accept the Bunsen values, the conditions being in Hempel's estimate C.° and 760.0 mm. at latitude 45° and the sea-level, while Bunsen's estimate is made in reference to Berlin, latitude 52° 31' 13'', and 41 meters above sea-level.

Special note.—In reference to the proportions of O₂ and N₂ in the air, of which the liter weight is given by Hempel, this may be said: "If one suppose this air to be by hypothesis water-free and at the standard

$$\begin{array}{rcl}
 7. & \text{Log } 1000^{\circ} & = 6.0000000 \\
 & \text{a. c. Log } 1292.2 & = 6.8886703 - 10 \\
 & & \hline
 & & 2.8886703 = \text{Log } 773.8742 \\
 8. & 1000 : 207.45 :: 773.8742 : \phi \\
 & \text{Log } 207.45 & = 2.3169134 \\
 & \text{Log } 773.8742 & = 2.8886703 \\
 & \text{a. c. Log } 1000 & = 7 \quad \quad \quad - 10 \\
 & & \hline
 & & 2.2055837 = \text{Log } 160.54 \\
 9. & 1000 : 792.55 :: 773.8742 : \phi \\
 & \text{Log } 792.55 & = 2.8990267 \\
 & \text{Log } 773.8742 & = 2.8886703 \\
 & \text{a. c. Log } 1000 & = 7 \quad \quad \quad - 10 \\
 & & \hline
 & & 2.7876970 = \text{Log } 613.334
 \end{array}$$

TABLE C. COMPOSITION OF ATMOSPHERIC AIR (STANDARD)
GRAMMES PER KILO.†

Bunsen	Berlin	231.8493 gm. O ₂	768.1507 gm. N ₂
Hempel	"	231.53097 " O ₂	768.46903 " N ₂
Hempel	Lat. 45 Seq.	231.4587 " O ₂	768.5413 " N ₂
Jolly	Not stated	229.5723 " O ₂	770.4277 " N ₂

temperature and pressure, then at Berlin the air must have contained 23.153097 per cent. O₂ by weight, and

$$\begin{aligned}
 & \dagger 1293.60 : 1000 :: 299.7909 : \phi \\
 & 1293.909 : 1000 :: 299.5913 : \phi \\
 & 1293.052 : 1000 :: 299.3923 : \phi \\
 & 1292.20 : 1000 :: 296.6535 : \phi \\
 & \text{Log } 1293.60 = 3.1118000 \quad \text{a. c.} = 6.8882000 - 10 \\
 & \text{Log } 1293.909 = 3.111903724 \quad = 6.888096276 - 10 \\
 & \text{Log } 1293.502 = 3.111767072 \quad = 6.888232928 - 10 \\
 & \text{Log } 1292.20 = 3.1113297 \quad = 6.8886700 - 10 \\
 & \text{Log } 299.7909 = 2.4768184 \\
 & \text{Log } 1000 = 3.0000000 \\
 & \text{a. c. Log } 1293.6 = 6.8882000 - 10 \\
 & \qquad \qquad \qquad 2.3650184 = \text{Log } 231.8493 \text{ O}_2 \\
 & \qquad \qquad \qquad \qquad \qquad \qquad 768.1507 \text{ N}_2 \\
 & \text{Log } 299.5913 = 2.47652915 \\
 & \text{Log } 1000 = 3 \\
 & \text{a. c. Log } 1293.909 = 6.888096276 - 10 \\
 & \qquad \qquad \qquad 2.364625426 = \text{Log } 231.53097 \text{ O}_2 \\
 & \qquad \qquad \qquad \qquad \qquad \qquad 768.46903 \text{ N}_2 \\
 & \text{Log } 299.3923 = 2.47624052 \\
 & \text{Log } 1000 = 3 \\
 & \text{a. c. Log } 1293.502 = 6.888232928 - 10 \\
 & \qquad \qquad \qquad 2.364473448 = \text{Log } 231.4587 \text{ O}_2 \\
 & \qquad \qquad \qquad \qquad \qquad \qquad 768.5413 \text{ N}_2 \\
 & \text{Log } 296.6535 = 2.4722494 \\
 & \text{Log } 1000 = 3 \\
 & \text{a. c. Log } 1292.20 = 6.8886700 - 10 \\
 & \qquad \qquad \qquad 2.3609194 = \text{Log } 229.5723 \text{ O}_2 \\
 & \qquad \qquad \qquad \qquad \qquad \qquad 770.4277 \text{ N}_2
 \end{aligned}$$

76.846903 per cent. N_2 , and at the sea-level 23.14587 per cent. O_2 and 76.85413 per cent. N_2 ." The results are not in agreement with the value of γ in the two places, and unless there is some remarkable mistake in the figures quoted here the statement of composition as shown by the liter weights demands some explanation. If the statement in the Hempel table in respect to specific gravity be used the liter weight of the atmosphere can be "worked back." When this is done it is clear that the table in Hempel contains a few strange mistakes, or that mixing of tables by compilers has produced fatal confusion in our data. It also shows the futility of trying to make the results of one series of experiments agree with any other set *until a suitable zero shall have been established*, say at Lat. 45° and sea level, and all our tables refigured to this location of the zero.

Case 5, representing the assembly of all conditions, can be discussed with propriety only when considering the water-saturated gas, and will be taken up under that head in suitable sections.

B. *The air being water-saturated.*— Having sufficiently considered the relations under the conventional conditions it is well now to consider those which we find under the natural ones, and to consider the changes in composition and certain other attributes impressed upon the air by changes in temperature, which cause changes in its water contents.

1. *The composition of one thousand volumes (liters or cubic meters) of gas, water-saturated.*

In considering the changes produced in the relative

quantities by the introduction of H_2O vapor into the volume of the gas, the tension of the water vapor at zero and at another temperature was incidentally given, that of the assumed temperature of the gas in the mains 12.6°C . The thermometric temperature of the barometer was given at 16°C ., for the sake of example, and to avoid the introduction of another quantity we in this discussion assume this as the temperature of the air.

On turning to Regnault's table of the tension of H_2O vapor (it is reprinted at the end of this book in the form given by Hempel, which differs slightly from other forms of the same table, *c. g.*, the form in which it is found in Bunsen), we find the tension of the "watery vapor" ("steam," H_2O), at 16°C . is given as 13.5103 mm. of mercury.

The proportional percentage of water in the air appears from the simple proportion, $760 : 13.5 :: 100 : X$, which is 17.8 c.c. per liter or liters per cubic meter more or less nearly.* Since this amount of watery vapor will displace a corresponding quantity of air, the two constituents retaining their relative proportions, the composition of the atmosphere becomes, if expressed in round numbers,

$$\text{H}_2\text{O} = 17.8$$

$$\text{O}_2 = 205.8$$

$$\text{N}_2 = 776.4$$

$$* \text{Log } 1000 = 3$$

$$\text{Log } 13.5103 = 1.13066406$$

$$\text{a. c. Log } 760.0 = 7.1191864 - 10$$

$$11.24985136 - 10 = \text{Log } 17.7768$$

liters per meter cube ; or if the percentage method of expression is chosen we may write

$$\text{H}_2\text{O} = 1.780$$

$$\text{O}_2 = 20.578$$

$$\text{N}_2 = 77.642$$

which is still an expression in parts per ten thousand quite as much as the other, and either one or the other may be taken to represent the composition of water-saturated air at C.° when the barometric height is 760 mm.

The effect of barometric changes.— The above difference between dry and saturated air undergoes variation in respect of temperature, and is variously supplemented and modified by barometric changes.

It must be remembered that temperature changes and barometric changes at times work together and at times oppose each other; thus when the barometer falls the volume of a given mass of air increases, which is likewise true if the temperature rises. In like way when the barometer rises or the thermometer falls the mass of air corresponding to a given volume increases. These two facts are fundamental data.

Barometric changes produce volume changes which are calculated according to Case 3 or 4 in Chapter I. (see page 13) for ascertaining the volume change depending upon barometric change, the temperature remaining constant.

As the barometric height in the case under discussion has been already assumed as 758.2 mm., the

increase in bulk will depend upon the proportion $758.2 : 760 :: 1.7768 : 1.782$,* in which 1.7768 is the space occupied by volume of H_2O vapor at 760.0 mm. pressure and 1.782 is the space occupied by volume of the same vapor at 758.2 mm. pressure.

From these data it follows that in the case under discussion the values just given

$$H_2O = 17.768$$

$$O_2 = 205.775$$

$$N_2 = 776.44$$

become

$$H_2O = 17.819$$

$$O_2 = 205.767$$

$$N_2 = \frac{776.414}{1000.000 \dagger}$$

parts per thousand when the water is considered.

Case 2. — The composition by weight of one thousand parts by volume.

In this case we meet with conditions in which the lack of a truly standard series of liter weights is a matter of utmost consequence, since in any attempt to determine values we must make use of liter weights of some

$$\begin{array}{rcl} * \text{ Log } 760 & = & 2.8808136 \\ \text{Log } 17.7768 & = & 1.24985136 \\ \text{a. c. Log } 758.2 & = & 7.1202162 - 10 \\ & & 11.25088116 - 10 = \text{Log } 17.8189 \\ & & \dagger 1000 - 17.8189 = 982.1811 \\ & & 1000 : 209.5 :: 982.1811 : \phi \\ \text{Log } 982.1811 & = & 2.992191584 \\ \text{Log } 209.5 & = & 2.3211840 \\ \text{a. c. Log } 1000 & = & 7.000 - 10 \\ & & 2.313375584 = \text{Log } 205.767 \end{array}$$

sort. The extent of the conflict of authorities is shown by the following: The liter weight of H_2O vapor, thermometer at 0°C. , and the barometer at 760.0 mm. is given by the following authorities, as follows in grammes per liter :

Bunsen at Berlin.....	0.8048
Von Jolly at Zurich (?)	0.8046
Hempel at Berlin.....	0.8046 (0.80458)
Hempel at sea-level, lat. 45°	0.8041 (0.80405)

the last decimal being omitted or forced according to the common practice.

As we made use of Hempel's 45° lat. values in the last chapter of calculations, which values are actually taken from Landolt and Bornstein, we may as well continue the use here, and we have for the cubic meter *weight* of H_2O -saturated air, at 0°C. and 760.0 mm. barm., but with the percentage composition of 16 $^\circ \text{C.}$:

17.78	liters H_2O	@	0.80405	gm.	@	liter	=	14.296	gm.
205.775	" O_2	"	1.42908	"	"	"	=	294.069	"
776.445	" N_2	"	1.25440	"	"	"	=	973.973	"

Hence 1 cubic meter of the atmosphere weighs 1,282.338 " in the conditions given, not in nature.

To obtain the weights for the specified barometric pressure we obtain first the values at 0°C. and 760.0 mm. pressure, preserving the percentage composition of 16 $^\circ \text{C.}$ and 758.2 mm. pressure ; hence the weights just obtained are in excess of the true weights, because a given bulk of air increases in all dimensions with an increase in temperature and therefore the mass in a given space is less. From all these considerations we deduce the following rule—*For finding the weights of any volumes of composite water-saturated gas, at any*

temperature and pressure, the composition and the liter weights of the components gases at C.° and 760.0 mm. pressure being known, said components being water-free:

(1) Find the percentages of the various components at the given temperature and pressure. (2) Multiply these percentages, expressed in liters, by the liter weights as given in the table. (3) Determine the space occupied by a liter, measured at 0 C.° and 760.0 mm. when the temperature changes to $0^{\circ} \pm N^{\circ} \text{ C.}$ and the pressure to 760.0 mm. $\pm M$. (If the temperature rises above zero the bulk will increase and the weight per cubic meter will be less, as will also be the case when the barometric pressure falls.) (4) Divide the weights obtained in (2) by the bulk obtained in (3) and the quotient will be the weight per cubic meter at the specified temperature and pressure.

To illustrate the above we give the solution of this problem, "What is the composition by weight per cubic meter at 16° C. and a barometer of 758.2 mm. of water-saturated air?"

Solution. — Temp. = 16 C.°. Barm. = 758.2. At 16 C.° the tension of H₂O vapor = 13.5103. Barm. = 760 mm. The volume corresponding to this tension when the barometer is at the standard pressure is found by the proportion $760 : 13.5103 :: 1000 : p$, and hence we may say that in the cubic meter of moist air are contained 17.7767¹ liters of H₂O vapor when the barometer is 760.0 mm., but when barometer falls this bulk increases and as it varies inversely as the pressure the proportion is as $758.2 : 760 :: 17.7767^2 : V^p$, which proportion gives for the value of V^p = volume of

watery vapor at barm. 758.2 17.8189 liters in a cubic meter. The sum of the oxygen and nitrogen will therefore be $1,000 - 17.8189 = 982.1811$ liters, and the relative amount will depend upon the assumed constants. Using those classed as "Hempel's" we have for the composition by volume of the moist air at temp. 16 C.°, barm. 758.2³ *

$$\text{H}_2\text{O} = 17.8189$$

$$\text{O}_2 = 205.7669$$

$$\text{N}_2 = 776.4142$$

$$1000.0000$$

$$* 1. 760 : 13.5103 :: 1000 : \phi$$

$$\text{Log } 1000 = 3$$

$$\text{Log } 13.5103 = 1.13066496$$

$$\text{a. c. Log } 760.0 = 7.1191864 - 10$$

$$\text{Log } \phi = 1.24985136$$

$$\phi = 17.7767 \text{ liters.}$$

$$2. 758.2 : 760 :: 17.7767 : \phi$$

$$\text{Log } 760.0 = 2.8808136$$

$$\text{Log } 17.7767 = 1.24985136$$

$$\text{a. c. Log } 758.2 = 7.1202162 - 10$$

$$\text{Log } \phi = 1.25088116$$

$$\phi = 17.8189 \text{ liters.}$$

$$3. 1000 - 17.8189 = 982.1811 \text{ liters.}$$

$$\text{Vol. O}_2 = 982.1811 \times 209.5 = 205.7669 \text{ liters.}$$

$$\text{Vol. N}_2 = 982.1811 - 205.7669 = 776.4142 \text{ liters.}$$

$$\text{Log } 0.9821811 = 9.992191595 - 10$$

$$\text{Log liters O}_2 209.5 \left. \begin{array}{l} \text{in dry air.} \end{array} \right\} = 9.3211840 - 10$$

$$19.313375595 - 20$$

$$= \text{Log } 0.2057669$$

$$= 205.7669 \text{ liters, O}_2.$$

$$\text{Log } 0.9821811 = 9.992191595 - 10$$

$$\text{Log liters N}_2 790.5 \left. \begin{array}{l} \text{in dry air.} \end{array} \right\} = 9.8979019 - 10$$

$$= 19.890093495 - 20$$

$$\text{Log } 776.4143 = \text{liters, N}_2.$$

which may be taken as the composition of 1,000 volumes. Having thus determined the composition of the air at the given temperature as measured on the Centigrade scale, and under the given barometric pressure we proceed as follows to determine the weight. Since it would be perfectly preposterous to try to form tables giving the weight of the various gases at a number of temperature points and under a number of pressures, although this has been proposed, the weight of each gas under the normal conditions has been observed and calculated with the greatest exactness.

For reducing the various quantities to normal conditions we make use of the formula given on page 15, as the one which applies when the gases are water-free, that is when as in this case the watery vapor is assembled as a special item. The formula will take the following form for reasons that will be perfectly obvious, the preceding pages having been properly studied,

$$V^o = V^t \times \frac{273}{273 + t} \times \frac{B}{760}$$

$$= V^t \times \frac{273}{289} \times \frac{758.2}{760} = V^t \times 0.9424^{1*}$$

$$\begin{array}{rcl} \text{H}_2\text{O} & = & 17.8189 \times 0.9424 = 16.793 \times 0.80405 = 13.5020 \text{ gm.} \\ \text{O}_2 & = & 205.7669 \times 0.9424 = 193.915 \times 1.42908 = 277.1195 \text{ gm.} \\ \text{N}_2 & = & 776.4142 \times 0.9424 = 731.692 \times 1.25440 = 917.8348 \text{ gm.} \\ & & \underline{1000.0000} \qquad \qquad \underline{942.400^2} \qquad \qquad \underline{1208.4563 \text{ gm.}^3} \end{array}$$

$$\begin{array}{rcl} * 1. \text{ Log } 273 & = & 2.4361626 \\ \text{Log } 758.2 & = & 2.8797838 \\ \text{a. c. Log } 289.0 & = & 7.5391022 - 10 \\ \text{a. c. Log } 760 & = & 7.1191864 - 10 \\ & & \underline{9.9742356 - 10 = \text{Log } 0.9424} \end{array}$$

This calculation shows that a cubic meter of water-saturated, *i. e.*, normal air at 16 C.° and bar. 758.2 mm. weighs 1,208.94 grammes more or less, or we may say a liter weighs 1.20894 grammes and a cubic meter 1.20894 kilos. Every step in the solution is given in full because I have noted when working with pupils that references do not refer and the least mistake in conception is a cause of endless confusion.

Case 3.—The composition by volume of 1,000 parts by weight.—This case finds almost daily expression in the query: "How much oxygen would there be in any unit weight of air, as pound or kilo?" Assume the same temperature and pressure as in the last discussed case and we have,

$$\begin{array}{rcl}
 2. \text{ Log } 17.8189 & = & 1.25088116 \\
 \text{Log } 0.9424 & = & 9.9742350 - 10 \\
 & & \underline{1.22511616} = 16.79254 \text{ liters} \\
 \text{Log } 205.7669 & = & 2.313375595 \\
 \text{Log } 0.9424 & = & 9.9742350 - 10 \\
 & & \underline{2.287610595} = \text{Log } 193.91464 \text{ liters} \\
 \text{Log } 776.4142 & = & 2.890093495 \\
 \text{Log } 0.9424 & = & 9.9742350 - 10 \\
 & & \underline{2.864328495} = \text{Log } 731.69233 \text{ liters} \\
 3. \text{ Log } 16.793 & = & 1.22511616 \\
 \text{Log } 0.80405 & = & 9.9052831 - 10 \\
 & & \underline{1.13039926} - 10 = \text{Log } 13.50204 \text{ gm.} \\
 \text{Log } 193.915 & = & 2.287610595 \\
 \text{Log } 1.42908 & = & 0.15505652 \\
 & & \underline{2.442667115} = \text{Log } 277.1195 \text{ gm.} \\
 \text{Log } 731.692 & = & 2.864328495 \\
 \text{Log } 1.2544 & = & 0.0984360 \\
 & & \underline{2.962764495} = \text{Log } 917.8348 \text{ gm.}
 \end{array}$$

$$\begin{aligned}
 a, 1208.4563 : 1,000 &:: \begin{cases} 17.8189 : 14.745 \text{ liters.} \\ 205.76699 : 170.27\bar{3} \text{ " } \\ 776.4142 : 642.484 \text{ " } \end{cases} \\
 b, 1208.4563 : 1,000 &:: 1,000.00 : 827.502^1 \text{ " } *
 \end{aligned}$$

From which we see that 1,000 grammes saturated air at the temperature 16 C.° and barometer 758.2 mm.

$$\begin{aligned}
 * 1. \quad & \text{Log } 1000 = 3 \\
 & \text{Log } 17.8189 = 1.25088116 \\
 & \text{a. c. Log } 1208.4563 = 6.917769032 - 10 \\
 & \quad \quad \quad 1.168650192 = \text{Log } 14.745\bar{18} \\
 & \text{Log } 1000 = 3 \\
 & \text{Log } 205.7669 = 2.313375595 \\
 & \text{a. c. Log } 1208.4563 = 6.917769032 - 10 \\
 & \quad \quad \quad 2.231144627 = \text{Log } 170.27\bar{26} \\
 & \text{Log } 1000 = 3 \\
 & \text{Log } 776.4142 = 2.890093495 \\
 & \text{a. c. Log } 1208.4563 = 6.917769032 - 10 \\
 & \quad \quad \quad 2.807862527 = \text{Log } 642.4843 \\
 & \text{Log } 1000 = 3 \\
 & \text{Log } 1000 = 3 \\
 & \text{a. c. Log } 1208.4563 = 6.917769032 - 10 \\
 & \quad \quad \quad 2.917769032 = \text{Log } 827.50\bar{2} \\
 2. \quad & \text{Log } 1000 = 3 \\
 & \text{Log } 13.5020 = 1.13039926 \\
 & \text{a. c. Log } 1208.4563 = 6.917769032 - 10 \\
 & \quad \quad \quad 1.048168292 = \text{Log } 11.173 \\
 & \text{Log } 1000 = 3 \\
 & \text{Log } 277.1195 = 2.442667115 \\
 & \text{a. c. Log } 1208.4563 = 6.917769032 - 10 \\
 & \quad \quad \quad 2.360436147 = \text{Log } 229.317 \\
 & \text{Log } 1000 = 3 \\
 & \text{Log } 917.8348 = 2.962764495 \\
 & \text{a. c. Log } 1208.4563 = 6.917769032 - 10 \\
 & \quad \quad \quad 2.880533527 = \text{Log } 759.511
 \end{aligned}$$

contains H_2O vapor, 14.848 liters, O_2 , gas, 170.182 and N_2 , gas, 642.141 liters, or in all 827.171 liters.

Case 4.—*The composition of one thousand parts by weight.*—Under the conditions of temperature and pressure specified this may be expressed,

$$1208.4563 : 1,000 :: \begin{cases} 13.5020 : 11.173 \text{ gm. } \text{H}_2\text{O}, \\ 277.1195 : 229.317 \text{ " } \text{O}_2, \\ 917.8348 : 759.510 \text{ " } \text{N}_2, \end{cases}^2$$

$$1208.4563 : 1,000 :: 1208.4563 : 1,000.000 \text{ gm. atmos.}$$

The conditions expressed under case 5, implying a reference to a normal not yet established can now be determined if the values of γ , gravity, and the two places are given, but this implies the discussion of the spheroidal envelope and it is not at present within the "gas manager's province."

Specific gravities and liter weights.—The specific gravities of all gases are taken with respect to an equal volume of atmospheric air as a unit, and these specific gravities are at present taken in not less than three ways: (*A*) The volume of the gas under investigation being at and being measured at 0°C. and 760 mm. pressure is compared with an equal volume of water-free air, the inquirendum being also water-free, and the air being at the normal temperature and pressure; or (*B*) the inquirendum being at atmospheric or other condition is compared with dry air at standard temperature and pressure; or (*C*) the inquirendum is compared with the atmosphere surrounding, and the temperature and pressure (*i. e.*, the density) of this temporary standard is made the subject of an inquiry later on.

All these methods are in daily use, the third chiefly for experiments, the first most commonly for calculations, and the second chiefly for comparing vapors under tension which are fluid at the standard temperature and pressure.

Almost a library has been written on this subject and there is simply endless confusion, due to the already so often mentioned fact there is no series of weights, physical attributes and units universally admitted to be the standards.

The definition of specific gravity. — This is distinct enough, but for some reason it is hard to waken a satisfactory sense of its importance. By definition, "specific gravity is the weight of a definite volume of any substance expressed in terms of the weight of the same volume of any other substance taken as unity." By convention it is agreed to add the following in the case of the specific gravity of gases, "both substances being of the same temperature at the same tension." This last is not essential, nor is it essential that the temperature shall be 0°C . and the atmospheric pressure shall be 760.00 mm., but these are usual as is the use of the weight of dry atmospheric air as the conventional unit of comparison as the standard weight.

A library could be filled with the lists of specific gravities and liter weights; nearly every book on chemistry has at least one such list, recklessly compiled; to make the list as long as possible being the apparent object of those responsible for them, and very frequently when calculations fail to come out right their

maker finds that the data which he has been using do not agree among themselves in many important regards.

For this reason it is well never to make use of a table for the data of a calculation until the quantities given have been subjected to a systematic investigation as to their trustworthiness and mutual dependence and agreement.

The standard lists. — The lists commonly found in use among gas men are three, or if we reckon the Hempel list as two lists, there are four of them. As has been said the list in Hempel is taken from another and less well known book, but it usually goes by Hempel's name. These authoritative lists are Bunsen's, the quantities calculated for Berlin, and many of them directly verified by weighing; Von Jolly's given by Winkler-Lunge, locality not stated and the two quoted by Hempel, but to which his name is usually attached as authority, one for Berlin the other for latitude 45° and the "sea-level," but the radius of the spheroid for this latitude is not given. The following table includes the liter weights and specific gravities of all the gases which are essentially needful for this inquiry. The note on page 112 of Hempel-Dennis says of the specific gravities and liter weights: "Most of these figures are from Landolt and Bornstein, 'Physikalisch-chemische Tabellen.' The liter weights are referred to Berlin." Which important fact is often lost sight of by users of his book.

TABLE IV.

GIVING SPECIFIC GRAVITIES AND LITER WEIGHTS OF VARIOUS GASES. THER. = 0 C.° BARM. = 760° mm.									
Quoted from.		Specific Gravity.	Liter Weights.	Liter Weights.	Specific Gravity.	Liter Weights, Lat. 45° E.	Liter Weights, At Berlin.	Adjusted Liter Weights.	Logs. of the Adjusted Liter Weights.
		Bunsen.	Bunsen.	Winkler.	Hempel.	Hempel.	Hempel.		
	<i>a</i>	<i>b</i>	<i>c</i>	<i>e</i>	<i>f</i>	<i>g</i>	<i>h</i>	<i>i</i>	<i>j</i>
1	Atmosphere.	1.0000000	1.2936	1.2922	1.000000	1.293052*	1.293909	1.293042	0.111612612
2	Oxygen.	1.1056	1.4303	1.4300	1.10521	1.42908	1.43003	1.42906	0.15595044
3	Nitrogen.	0.9713	1.2566	1.2562	0.97010	1.25440	1.25523	1.25440	0.0984360
4	Hydrogen.	0.0692	0.0896	0.0896	0.069234	0.089523	0.089582	0.08952	8.9512101
5	Water.	0.6221	0.8048	0.8046	0.62182	0.80405	0.80458	0.80405	9.9052831
6	Carbon.	0.8292	1.0727	(1.0722)				1.07194	0.0301705
7	Carbonic Oxide.	0.9674	1.2515	1.2512	0.96709	1.25050	1.25133	1.25050	0.0970837
8	Carbonic Acid.	1.5202	1.9666	1.9663	1.51968	1.96503	1.96633	1.96503	0.29336923
9	CH ₄ .	0.5531	0.7155	0.7154	0.55297	0.71502	0.71549	0.71501	9.8543121
10	Methane.	0.9678	1.2520	1.2517	0.96744	1.25095	1.25178	1.25097	0.1000533
11	C ₂ H ₄ .	1.4512	1.8773	1.8775	1.45118	1.87644	1.87769	1.87647	0.2734164
12	Propylene.	1.9355	2.5038	2.5034	1.93488	2.50190	2.50355	2.50196	0.39828034
13	Butylene.	2.6944	3.4856	3.4864				3.48433	0.5421255
13	Benzene.								

* This weight is impossible as it makes the composition of the air 0.2213 oxygen. The value 1.29 in column (*i*) corresponds to the most probable composition under normal conditions and corresponds to the value required for the specific gravity of oxygen and nitrogen as given in this table. (Air = 0.20952 O₂ and 0.79048 N₂).

CHAPTER III.

COMBUSTION, REQUIREMENTS AND PRODUCTS.

THE process next to be considered is that by which the gas is used, it is burned. That is to say, it is caused to unite with oxygen, entering thereby, by this process of combustion, into new chemical unions, by which the identity of the chemical compounds is lost. The new chemical compounds disappear in the great atmospheric mass to undergo once more the myriad changes which make up the existence cycle of the universe of force and matter.

The first act in this series of processes is the breaking up of the existing unions among the atoms of the constituent molecules by heat. It may be that the heat is that of a match as in the familiar act of lighting the gas at the fixture, or with the electric spark in the only less familiar gas engine. This ignition by the heat thus produced causes motion among the atoms of the molecules, which destroys the existing grouping, freeing the atoms, which in turn reunite to form new molecules, it may be new hydrocarbons to be again destroyed, or oxygen unions, giving water and carbon dioxide, the ultimate forms. The question of which union will occur depends for its answer on the amount of oxygen which chances to be in contact with the mass, so to say, of the gas molecules at the moment of rupture and to be in a condition to unite with them.

In their last expression these unions are two oxides both well known, one being water, hydrogen oxide; speaking accurately the neutral oxide or hydrogen hydrate HOH, commonly, but incorrectly, written H_2O , and carbon dioxide, commonly called carbonic acid gas and written CO_2 in chemical notation. More correctly perhaps this should be written and regarded as the anhydride of carbonic acid, H_2CO_3 .

It follows then that for combustion to attain perfection we need the fuel to burn, in this case the illuminating gas which we are considering, and the oxygen to be used in sustaining the combustion, which combustion is in fact the chemical union, and third the igniting agent, the heat which by disturbing the existing unions makes new ones possible. This union with oxygen is accompanied by liberation of energy which will become sensible in the form of heat or light according to the circumstances and surrounding conditions at the time, but considered mechanically it is simply a series of vibrations of the ether produced by the interaction of the various atoms of carbon, hydrogen and oxygen in their transition to the new grouping from the previous one. No matter how it may become evident to our senses the fact is as has been so often stated; it is simply a mode of motion which we are considering.

This mode of motion produces a reaction which we are able to measure in a way; we speak of it as the amount of heat, and this amount of heat may be discussed as the amount produced per unit of weight or the amount produced per unit of volume. In the discussion which follows the values for the various ingredients found in

illuminating gas are considered by both systems, the valuation by weight and the valuation by volume.

The combustion values by weight and by volume. —

In evaluating the quantities under this heading we consider the combustible components of the gas, excepting the CO component, simply as so much carbon and so much hydrogen, that is as reduced to their constituents, and reckon these *seriatim*. In the CO component we consider the carbon only. This we do rightly, for the very first act of combustion is the disruption of carbon-hydrogen molecules, and throughout the flame the action of these two constituents of the hydrocarbon gases is as if they had been mixtures from the beginning and never had been in combination. It is because the disruption of the molecules takes up energy that the available heat of the molecule is less than that of its constituents. (See next chapter.)

The gases which we must consider are those which appear in the analysis by the Hempel method, viz., H_2 , CH_4 , C_2H_4 , C_6H_6 and CO.

Isomeres are present, but as they do not appear in the Hempel procedure they will not in the report and in this connection they need not be considered. The values required for the discussion are all to be found in Table IV., column *i*; the values given are obtained by refiguring from the data given in the table itself.

Hempel gives the liter weight of oxygen, O_2 , as 1.42908 grammes and that of carbon monoxide as 1.25050 grammes. Therefore the weight of the carbon gas is

$$\left(1.25050 - \frac{1.42908}{2}\right) \times 2 = 1.07192 = C_2.$$

TABLE V.
THE REQUIREMENTS FOR AND PRODUCTS OF COMBUSTION OF A UNIT VOLUME, BY MEASUREMENT
AND BY WEIGHT.

Names of the Ingredients of Illuminating Gas, (Hempel.)	Symbols	Liter Weights* Lat. 45° and Bar. = 760.0 Ther. = 0°C.	Proportion by Vols.		Weights of Constituents.		Oxygen Required for Perfect Combustion.		Water Produced from Perfect Combustion.		Carbonic Acid from Perfect Combustion.		Symbols
			H ₂	C ₂	Hydrogen, gms. or kilos.	Carbon, gms. or kilos.	By Vol.	By Weight.	By Vol.	By Weight.	By Vol.	By Weight.	
Carbon monoxide.	CO	1.25050		1/2		0.53596	1/2	0.71454			1	1.96504	CO
Hydrogen.	H ₂	0.089523	1		0.089523		1/2	0.71454	1	0.804063			H ₂
Marsh gas.	CH ₄	0.715006	2	1/2	0.179046	0.53596	2	2.85816	2	1.608126	1	1.96504	CH ₄
Ethylene.	C ₂ H ₄	1.250966	2	1	0.179046	1.07192	3	4.28724	2	1.608126	2	3.93008	C ₂ H ₄
Benzene.	C ₆ H ₆	3.484329	3	3	0.268569	3.21576	7 1/2	10.71810	3	2.412189	6	11.79024	C ₆ H ₆

* Adjusted values. Table IV., column i.

Hence the liter weight of

$$\begin{aligned}\text{CH}_4 &= \left(\frac{\text{C}_2}{2} + 4 \frac{\text{H}_2}{2} \right) \\ &= \frac{1.07192}{2} + \frac{0.358092}{2} = 0.715006.\end{aligned}$$

The same process gives for C_2H_4 the liter weight of 1.250966 grammes. These liter weights give results which will balance, the others do not. Using this same process of analysis but the values given for CO and CO_2 , we obtain a somewhat variant value. Using these quantities and representing the value (weight) of carbon by x and that of oxygen by y we obtain pairs of equations which if the values (weights) of the two carbon oxides are correctly given leave nothing in doubt.

These equations and the solutions are as follows:

1. Using Bunsen's values,

$$(a) \quad x + y = 1.2515,$$

$$(b) \quad x + 2y = 1.9666,$$

subtracting a from b , $y = 0.7151$; hence O_2 weighs 1.4302 grammes. Multiplying a by 2 and subtracting $x = 0.5364$, hence C_2 weighs 1.0728 grammes.

2. Winkler's data developed by the same method give as results, O_2 weighs 1.4302 grammes and C_2 weighs 1.0722 grammes.

3. Hempel a . O_2 weighs 1.42906, C_2 , 1.07194.

4. Hempel b . O_2 weighs 1.43000, C_2 , 1.07266.

To avoid the inevitable confusion if the whole series of values were used indiscriminately a special series of quantities has been figured as stated in the note to the table and these are used in all the calculations which follow.

TABLE VI.
THE REQUIREMENTS FOR AND PRODUCTS OF THE COMBUSTION OF A GAS SAMPLE BY WEIGHT.

Amounts of the Constituent Gases in Sample. (Hempel.)	Symbols.	Product of Liter Weights by Amounts in Sample.	Proportional Volumes.		Weights of Constituent Parts.		Oxygen Required for Perfect Combustion.		Water Produced from Perfect Combustion.		Carbonic Acid from Perfect Combustion.		Symbols.
			H ₂	C ₂	Hydrogen. Gms. @ Cubic Meter.	Carbon Gms. @ Cubic Meter.	By Weight.	By Weight.	By Weight.	By Weight.	By Weight.	By Weight.	
99.6 L.	CO	124.5498				53.381616	1/2	71.168184			1	195.717984	CO
452.4 "	H ₂	40.500205	1		40.500205		1/2	323.758101	1	364.258306			H ₂
301.6 "	CH ₄	215.645810	2	1/2	54.000274	161.645536	2	862.021056	2	485.010802	1	592.656064	CH ₄
43.4 "	C ₂ H ₄	54.291924	2	1	7.770596	46.521328	3	186.066216	2	69.792668	2	170.565472	C ₂ H ₄
5.9 "	C ₂ H ₆	20.557541	3	3	1.584587	18.972984	7 1/2	63.236790	3	14.231915	6	69.562416	C ₂ H ₆

Since the values correspond with those of a unit weight or volume it is perfectly clear that the values for any weight or volume will be obtainable by the simple process of multiplying by the number of units in weight or volume.

If we multiply the figures of the analysis given on page 8 (Table II., Chapter I.) by the amounts in this Table V. we obtain the next needed series of data, Table VI.

These for practical use must be brought to the values which they have at the temperatures and pressures of the gas in the mains at the time when the specimen was taken for observation, or to that of the atmosphere at that time according to the purpose for which it is intended to use them.

Strictly speaking the barometric pressure should be increased by the tension of the gas in the mains, but since the gas becomes useful not in the mains but at the instant of exit from the fixture we really have but one set of values, to be considered in the following pages.

It is of course understood that the gas at the moment of exit is at the atmospheric tension and at the temperature of the mains. We will consider the condition at the moment of exit.

The amount of air required for the combustion of the gas under the conditions of the moment of exit. —
Barometer 758.2 mm., temperature 16° C.

The table just given gives the weights at zero and at the normal pressure; from this it follows that two courses are open to us. We may reduce each item by

itself and make a new table of values or we may regard the footing only and reduce that. On examination and footing we find that the total oxygen required is a trifle more than 1,506.25 grammes, and turning to the analysis on page 2 we see that the gas carries a small content — 3 parts per 1,000 or 3 liters @ cubic meter. This value multiplied by the weight @ liter is 3×1.42908 grammes = 4.28724 grammes per meter cube or 4.3 grammes nearly to bring it to convenient form. The value is so small as compared with the total required that it may be neglected and we may say "to burn one cubic meter of this gas at zero requires in all 1,506.25 grammes O_2 at zero." We may convert this by saying 1,506.25 grammes = 1,054 liters per cubic meter ($1,506.25 \div 1.42908 = 1,054$), which on the basis of Hempel's per cent. of O_2 in the air represents $1,054 \div 0.2095$ or 5,031 liters of dry air per meter cube; or by making use of the Bunsen value 20.96 per cent. O_2 in air and his weight for oxygen @ liter (1.4303 grammes), the amount of *air* required at 0 C.° and 760 mm. will be 5,024.3 liters. So that for practical purposes the volume of air required may be given as 5,028 liters.

The volume at temperature 16 C.° and barometer 758.2 will then be found by case 6, page 17,

$$V' = V^o \times \frac{273 + t}{273} \times \frac{760}{B - f},$$

which in the conditions named becomes

$$V' = V^o \times \frac{289}{273} \times \frac{760}{744.7} = V^o \times 1.08 \text{ nearly.}$$

Hence using the Hempel value 5,433.5 liters will be needed, or according to Bunsen 5,426.24 liters of atmospheric air at the atmospheric temperature and pressure.

Simple as this calculation is the direct estimate by volume is still more simple. The data are as follows:

The products of combustion are of two distinct sorts. The ponderable substances investigated by the science of the chemist, and the imponderable forces which enter the domain of physics. To the first belong water and carbon dioxide, to which as the last term every organic substance may be considered to be reduced, to the second light and heat which we now recognize as modes of motion.

The amount of carbon dioxide produced, measured both by weight and volume, may be indicated in two ways, one in grammes the other in liters.

Thus following the plan already used we find the total weight at 0° C. and 760 mm. to be for the water 933.3 grammes, and for the carbon dioxide 1,028.5 grammes, or expressed in volumes H_2O 1,160.1 liters @ cubic meter of gas burned and CO_2 523.4 liters. These are the amounts of the footings in the table expressed to the nearest decimal.

Another important point to be considered is the compression in volume. It will be seen at a glance that the weights of the H_2O and CO_2 items taken together are equal to the weight of the fuel plus the weight of the oxygen O_2 used in combustion, but the bulk of the gas does not agree for the sum expressing the amount in bulk of the H_2O and CO_2 in gaseous

TABLE VII.

THE REQUIREMENTS FOR AND THE PRODUCTS OF THE COMBUSTION OF A GAS SAMPLE BY VOLUME.

Amounts of the Ingredients in the Sample. (Hempel).	Volumes.		Volumes in Sample.		Oxygen Required for Perfect Combustion.		Water Produced by Perfect Combustion.		Carbonic Acid Gas from Perfect Combustion.		Sym-bols.
	H ₂	C ₈	Hydrogen.	Carbon.	By Vol.	By Liters @ Cubic Meter.	By Vol.	By Liters @ Cubic Meter.	By Vol.	By Liters @ Cubic Meter.	
99.6 L.		1/2	452.4 L.	49.8 L.	1/2	49.8 L.			1	99.6	CO
452.4 "	1		603.2 "	150.8 "	1/2	226.2 "	1	452.4 L.			H ₂
301.6 "	2	1/2	86.8 "	43.4 "	2	603.2 "	2	603.2 "	1	301.6	CH ₄
43.4 "	2	1	17.7 "	17.7 "	3	130.2 "	2	86.8 "	2	86.8	C ₂ H ₄
5.9 "	3	3			7 1/2	44.25 "	3	17.7 "	6	35.4	C ₆ H ₆
Oxygen required for combustion, vol. dry o° C., 760.0 mm. 1,053.65 L.											
Water from combustion liters, vapor, 1,160.1 L.											
Carbon dioxide from combustion, gas, 3,973.30 L.											
Nitrogen corresponding to above as per Bunsen, 5,026.96											
Total dry air at o° C. and 760.00 mm. 5,234.4 L.											

form is only about $\frac{5}{8}$ of the gases concerned in combustion.

These weights and volumes are at zero C., and at the assumed normal pressure and to convert them we make use of the process developed before and multiplying the bulks of water and carbon dioxide by 1.08 we obtain as the bulk of the products of combustion CO_2 565.3 c.c., H_2O 1,252.9 c.c., and the air demand becomes 5,429.11 c.c.

Sometimes it is well to consider all the items in detail, sometimes they may be taken in groups, at other times it may seem difficult to make out a full statement of all items without producing confusion, but by the use of a blank statement ruled as the following all items can be brought into view in the simple way which has been discussed in the previous pages. This is so important for many needs that it would be for the convenience of the manager of the works if he had such a table made out as part of the daily routine.

TABLE VIII.
THE REQUIREMENTS FOR AND THE PRODUCTS OF THE COMBUSTION OF A GAS SAMPLE BY VOLUME.

Amounts of the Ingredients in the Sample (Hempel).	Sym- bols.	Volumes.		Volumes in Sample.		Oxygen Required for Perfect Combustion.		Water Produced by Perfect Combustion.		Carbonic Acid Gas from Perfect Combustion.		Sym- bols.
		H ₂	C ₂	Hydrogen.	Carbon.	By Vol.	By Liters @ Cubic Meter.	By Vol.	In Liters @ Cubic Meter.	By Vol.	In Liters @ Cubic Meter.	

Oxygen required for combustion, vol. dry 0° C., 760.0 mm.

Water from combustion liters, vapor,

Carbon dioxide from combustion, gas,

Nitrogen corresponding to above as per Bunsen,

Total dry air at 0° C. and 760.00 mm.

CHAPTER IV.

THE IMMATERIAL PRODUCTS OF COMBUSTION.

WHEN a gas is burned it produces heat, a mode of motion ; it also incidentally produces light, another mode of motion, by heating any solid which may chance to be present and in a way to be heated. When a nearly perfect burner is used with a first-class mantle the light given by the mantle can be expressed by an equation containing the total energy of a given weight of gas as one variable, the weight of mantle as another variable and the specific heat of the mantles as a constant.

We may also express the known facts much more explicitly by saying that 1,000 B.T.U. developed in a gas flame will produce from 96 to 108 B.A. units of light with most of the first-class mantles.

We may also give expression to the value of gas as a fuel for gas engines in terms of the B.T.U. resulting from its combustion. It therefore follows that the important question to be considered is what is the potential energy of a given sample of illuminating gas per unit of weight or space. To answer this we must consider a number of things in reference to combustion, and first among them, what is the total amount of heat obtainable from the combustion of the gas in gross ?

This is easily determined by the simple multiplication of the number of grammes of carbon present in

the given bulk of gas, in the form in which it can be burned, by the heat value of one gramme, and the number of grammes of hydrogen by the heat value of one gramme, and then taking their sum. But before we take the value of hydrogen from the table we must stop to consider that to give the values in some tables the water must be supposed to have been cooled to zero, this being the point to which all is referred.

When the watery vapor is cooled only to 100° C. it remains a gas, but if cooled to water at 100° C. it obeys another law. At the same time in reckoning the gross production of heat, or the maximum potential energy to use a better phrase, we must consider the products of combustion to be thus cooled. This being premised we may take into consideration but few quantities, remembering only that we must not confuse the two values given for water :

$$\begin{aligned}
 m \text{ gms. H}_2 \times \text{heat of combustion to } 0^{\circ} \text{ C.} &= A \\
 &= m \times 34.462 \text{ Bunsen.} \\
 &= m \times 34.180 \text{ Winkler.} \\
 n \text{ gms. C}_2 \times \text{heat of combustion to } 0^{\circ} \text{ C.} &= B \\
 &= n \times 8.080 \text{ Bunsen.} \\
 &= n \times 8.0473 \text{ Winkler.} \\
 m \text{ gms. H}_2 \times \text{heat of combustion at } 100^{\circ} \text{ C.} &= C \\
 &= m \times 28.890 \text{ Bunsen.} \\
 &= m \times 28.780 \text{ Winkler.*}
 \end{aligned}$$

In these quantities the unit is the calorie (K), the amount of heat required to raise one kilogramme of water one degree in the Centigrade scale. Some other

* To convert 1 gm. of H_2O at 100° C. into steam at 100° C., that is into water gas, requires 537 calories, according to the table in the Winkler-Lunge 5.4 calories. If we start with water at the ordinary temperature, say 20° , 80 calories more will be required.

conditions obtain, but they need not be discussed here. Oftentimes it is more convenient to express this quantity of heat by a term dependent upon volume. Thus we may say,

$$\begin{aligned}
 q \text{ liters } H_2 \times \text{heat of combustion to } 0^\circ \text{ C.} &= D \\
 &= q \times \begin{cases} 3.0879 \text{ Bunsen.} \\ 3.06191 \text{ Winkler.} \end{cases} \\
 r \text{ liters } C_2 \text{ (gas)} \times \text{heat of combustion to } 0^\circ \text{ C.} &= E \\
 &= r \times \begin{cases} 8.6671 \text{ Bunsen.} \\ 8.63202 \text{ Winkler.} \end{cases} \\
 q \text{ liters } H_2 \times \text{heat of combustion to } 100^\circ \text{ C.} &= F \\
 &= q \times \begin{cases} 2.5863 \text{ Bunsen.} \\ 2.57817 \text{ Winkler.} \end{cases}
 \end{aligned}$$

We may apply both of these statements directly to the specimen of gas which we have been discussing, and obtain some figures which are full of meaning, not only from the standpoint of the special occupation, but also from the one of science at large. The weights are those given by taking the sum of the weights of hydrogen and carbon given in Table VI., or of the items in line in Table VIII.

$$\begin{aligned}
 \text{A. } 104.86 \text{ gms. } H_2 \times 34.462 &= 3613.68532 \text{ cal. Bunsen.} \\
 &\quad \times 34.180 = 3583.1148 \text{ " Winkler.} \\
 \text{B. } 280.52 \text{ " } C_2 \times 8.080 &= 2266.6016 \text{ " Bunsen.} \\
 &\quad \times 8.0473 = 2257.4286 \text{ " Winkler.} \\
 \text{C. } 104.86 \text{ " } H_2 \times 28.89 &= 3029.4054 \text{ " Bunsen.} \\
 &\quad \times 28.780 = 3017.8708 \text{ " Winkler.}
 \end{aligned}$$

From which it appears that the total available heat when all combustion products are cooled to 0° C. is, by Bunsen's reckoning, 5,880.29 calories, by Winkler's 5,840.54 calories, or when the steam remains steam 5,296.01 calories, Bunsen and 5,275.30 calories Winkler.

If we intend to obtain the total amount available for use in heating in say one cubic meter, we must con-

sider not only the heat credit but also the heat debit, otherwise we shall have credited the gas with a great amount of potential energy which really is not available for use, viz., the amount expended in the total interior work of the flame. For instance, some compounds like methane give out more heat when burned than is obtained by the combustion of the constituents of methane, carbon and hydrogen in the free state. Other compounds, benzene, acetylene and ethylene, for instance, give out less heat than the free elements of which they are composed. These errors tend therefore to counterbalance each other in the method of calculation already given.

These errors may be entirely eliminated if the heat of combustion of each constituent is obtained by multiplying the heat of combustion per cubic meter of that constituent by the number of meters present and taking the sum of these results to obtain the heat of combustion of the gas in question. The method of making this calculation is indicated in the following table :

TABLE IX.
HEAT OF COMBUSTION OF A GAS CALCULATED FROM THE HEAT OF COMBUSTION OF THE CONSTITUENTS.

Constituents of the Gas.	No. of Liters Per Cubic Meter.	Heat of Combustion Per Cubic Meter.	Heat of Combustion of Each Constituent.
Carbon Monoxide, CO.	99.6 L	3057	304.5
Hydrogen, H ₂ .	452.4 "	3066	1387.06
Methane, CH ₄ .	301.6 "	9340	2816.9
Ethylene, C ₂ H ₄ .	43.4 "	14980	650.13
Benzene, C ₆ H ₆ .	5.9 "	44372	251.8

Total heat of combustion per cubic meter, 5410.37

In reckoning the available heat of combustion of the hydrocarbon gases it follows inevitably that in practice we must determine the temperature of the gases at the exit if we intend to know how much heat is in fact available. For example, if in a gas stove we are burning say 5 cubic feet per hour, in order to determine how much heat is available for heating the air in the room we must know the gross amount of heat produced by combustion, and the temperature of the discharged gases, and then having calculated the heat which they carry off we can determine the difference which is the amount available for work, for the purpose of heating the room.

To determine the amount of heat carried away by the gas we multiply the mass of the gas, determined by its weight, by the specific heat of that gas into the number of degrees above zero. It is needful therefore to remember that when we speak of the specific heat we mean "the amount of heat, expressed in calories, required to raise the unit mass through one degree of the Centigrade scale."

There are two series of quantities answering to this definition, one in which the pressure on the gas remains constant and the volume increases, the other in which the volume remains constant. It is with the first of these, the specific heat under constant pressure, with which we are just now concerned.

Classic values. — For modern official values (Smithsonian tables) see Table XII., page 64.

From these quantities, which are for mass, not for volume, the so-called volumetric specific heats are ob-

TABLE X.
SPECIFIC HEAT OF GASES. WEIGHT AND VOLUME.

Designation of Gas.	Symbol.	Regnault's Value. (Bunsen "Methoden" (1877) p. 310.)	Weight in Kilograms of Meter Cube.	Specific Heat by Volume.	Symbol.
Atmosphere.		0.2370	1.290	0.30573	
Oxygen.	O ₂	0.2182	1.42908	0.311825	O ₂
Nitrogen.	N ₂	0.2440	1.25440	0.306074	N ₂
Hydrogen.	H ₂	3.4046	0.089523	0.304790	H ₂
Carbonic acid.	CO ₂	0.2164	1.96504	0.425235	CO ₂
Carbonic oxide.	CO	0.2479	1.2505	0.309999	CO
Marsh gas.	CH ₄	0.5929	0.715006	0.423927	CH ₄
Ethylene.	C ₂ H ₄	0.3694	1.250966	0.462107	C ₂ H ₄
Water.	H ₂ O	0.4750	0.804063	0.381930	H ₂ O
Acetylene.	C ₂ H ₂	1.26	1.1638		C ₂ H ₂
Benzol.*	C ₆ H ₆	0.2631	3.484329	0.916727	C ₆ H ₆

tained by dividing the amounts of heat per kilo. by the weights per meter cube. It will be noted how nearly they approach to a constant quantity, or rather that the gases tend to form two groups.

The last items wanting from Bunsen's (Regnault's) list, but figured from various data, seemed at one time to answer to the facts of the case very nearly.

It should be remembered that benzol (benzene) is, so far as illuminating gas is concerned, in much the same relation that water is to the air. In using the above coefficients it is well to disregard the value for "air," which is here assumed to be dry, and when the value of air is wanted to consider the oxygen fraction, the nitrogen fraction and the water fraction, each by itself, and then to take the sum; this will save many mistakes.

* This value is none too certain and probably is *not* correct, at best only approximately right, and probably much too small. See values for Benzol, Table XII., page 64.

Knowing the total amount of heat available from the combustion of a cubic meter of gas we may determine the balance remaining when the next cubic meter has been heated to the ignition point, the difference between these two will give the *amount* of heat, expressed in calories or in B. T. U. (British thermal units), or (2) we may ignore the next cubic meter, and assume that the whole of the heat is expended endothermically, in the meter just burned, or (3) we may discuss the flame temperature assuming no loss of heat by reason of work.

Many other points might be suggested for investigation — but these are primary considerations demanding attention day by day, and they underlie many important possible contingencies.

We have determined the total amount of heat produced by burning a cubic meter of the gas which we have been discussing. To determine the other items it is essential to know the specific heat of the special gas mixture which we have been considering. To do this we must obtain the specific heat of the ingredients and take their sum.

We start from the statement of the composition of the dry gas at zero, continuing as below, setting against each item its specific heat by volume, and multiplying, remembering the position of the decimal point, and we thus obtain expressed in fractions of a calorie the amount required and their sum represents the *volume-metric* specific heat of the gaseous mixture.

If now the total heat of combustion as given on page 57 be divided by this requirement per degree

TABLE XI.

SPECIFIC HEAT OF ILLUMINATING GAS MIXTURE BY VOLUME AND BY WEIGHT, WITH AIR FOR COMBUSTION.*

Ingredient.	$\frac{a}{\text{Symbol.}}$	$\frac{b}{\text{Specific Heat by Volume.}}$	$\frac{a \times b}{\text{Specific Heat of Amount in Gas.}}$	$\frac{c}{\text{Amount in Cubic Meter.}}$	$\frac{d}{\text{Weight @ Cubic Meter.}}$	$\frac{e = c \times d}{\text{Amount by Weight.}}$	$\frac{f}{\text{Specific Heat by Weight.}}$	$\frac{e \times f = g}{\text{Specific Heat of Amount in Gas.}}$	Symbol.
1. Hydrocarb. Vap.	H_2C_6	0.006	0.916727	0.006	3.484329	0.020906	0.2931	0.005500	C_6H_6
2. Carb. dioxide.	CO_2	0.034	0.425235	0.034	1.96504	0.066811	0.2164	0.014458	CO_2
3. Heavy Hydroc.	C_2H_4	0.044	0.462107	0.044	1.250966	0.055044	0.3694	0.020333	C_2H_4
4. Oxygen.	O_2	0.003	0.311825	0.003	1.42908	0.004287	0.2182	0.000935	O_2
5. Carb. monoxide.	CO	0.101	0.309999	0.101	1.25050	0.126301	0.2479	0.031310	CO
6. Hydrogen.	H_2	0.459	0.304790	0.459	0.089523	0.042091	3.4046	0.139899	H_2
7. Methane.	CH_4	0.306	0.423927	0.306	0.715006	0.218792	0.5929	0.129722	CH_4
8. Nitrogen.	N_2	0.047	0.306074	0.047	1.2544	0.058957	0.244	0.014386	N_2
Total specific heat of mixture by volume.			0.356543				By weight.	0.356543	

Specific gravity = 0.5932/1.29 = 0.4598.

Weight @ cu. m. 0.593189 kil. @ cu. m.

SPECIFIC HEAT OF ATMOSPHERIC AIR FOR COMBUSTION AS ABOVE.

1. Oxygen.	O_2	1.069	0.311825	0.333341	O_2	1.069	1.42908	1.527687	0.2182	0.333341	O_2
2. Nitrogen.	N_2	4.02407	0.306074	1.231663	N_2	4.02407	1.2544	5.047794	0.2440	1.231662	N_2
Total specific heat of needed air by vol.				1.565004							
Total specific heat of mixture.				1.921547							

Weight of air per cubic meter 6.575481 K., say 6.6 K. air per cubic meter of gas burned, or 1 gas 11 air by weight.

* Air and gas are both assumed to be water-free.

obtain the total maximum increase in temperature assuming (*a*) that no heat is lost in radiation, but (*b*) the heat is to some extent transformed into *work* in that the gas expands since the constants used are those of *uniform pressure* and *not* those of uniform volume. Dividing the values on page 57 we obtain, if Winkler's values be used, and all products are taken at 0° C., as the combustion temperature $3,046.5^{\circ}$ C. and under the same conditions from the Bunsen values $3,060.115^{\circ}$ C. as the equivalent temperature. In one sense these values are meaningless and useless, but in another sense they are important and practical for they indicate to those who stop to consider them that there is a limit not so far beyond our best modern practice at which no further advance in heating furnaces with hydrocarbons is possible. But in practice both gas and air are water-saturated, which makes a wide difference between the temperature just given and the highest obtainable in practical life.

It is possible however that the gas manager may not be satisfied with this rendering of the results, but instead may wish for the most accurate rendering obtainable; if so he will wish to consider all the facts and in all probability will wish to use another set of values in place of those in Table X., which have been so often questioned.

If he wishes the last refinement he can use this table below, Table XII., for the heat constants, and, having considered the various effects of moisture under the local conditions, will produce for his daily record a statement corresponding to Table XIII., which con-

tains all the data which are needed for the fullest statement.

TABLE XII.

THE SMITHSONIAN (OFFICIAL) CONSTANTS. (SPECIFIC HEAT.)

Ingredient Name.	Symbol	Specific Heat by Weight.	Weight per Cubic Meter.	Specific Heat by Volume.	Symbol
Atmosphere.		0.23788	1.290	0.306866	
Oxygen.	O_2	0.2182	1.250966	0.272962	O_2
Nitrogen.	N_2	0.2438	1.254400	0.305725	N_2
Hydrogen.	H_2	3.4062	0.089523	0.304933	H_2
Carbonic acid.	CO_2	0.2012	1.96504	0.395362	CO_2
Carbonic oxide.	CO	0.2426	1.25050	0.302674	CO
Marsh gas.	CH_4	0.5929	0.715006	0.423924	CH_4
Ethylene.	C_2H_4	0.3694	1.42908	0.527902	C_2H_4
Water.	H_2O	0.4296	0.804063	0.345425	H_2O
Benzol.	C_6H_6	0.3325	3.484329	1.157524	C_6H_6

It will be noted that in the procedure needed here the first step is the reduction of the constants of the specimen to those of water-saturated gas and air, at the standard temperature and pressure (to 0° C. and 760.0 mm. pressure), *not* to dry air.

It will be noted that the formula to be used is

$$V^o = V^r \times \frac{273}{273 + t} \times \frac{760}{P^m - d}$$

and not

$$V^o = V^r \times \frac{273}{273 + t} \times \frac{760}{P^m},$$

because it is *not* dry gas but water-saturated gas which we are dealing with in both cases.

Having obtained the value equivalent to the given volume we can construct the table, as follows ;

TABLE XIII.

SPECIFIC HEAT OF MIXTURE OF ILLUMINATING GAS AND AIR FOR COMBUSTION ACCORDING TO OFFICIAL CONSTANTS.

Names of the Constituents.	Volumes of Ingredients Gases.	Same at Standard Temp. and Pressure.	Specific Heat @ Unit Volume of Constituents.	Specific Heat of Component Volumes.	Volumes of Ingr. at Stand. and Temp. Pressure.	Weight of Ingr. @ Meter Cube.	Weight of Constant Volumes.	Specific Heat by Weight.	Specific Heat of Ingredients by Weight.
Watery vapor.	H ₂ O	0.0143	0.013636	0.345425	0.004710	0.013636	0.804063	0.010965	0.004710
Hydrocarb. vapors.	C ₂ H ₆	59	5626	1.157524	6518	5626	3.484329	0.019604	6518
Carbon dioxide.	CO ₂	335	31946	0.395362	12630	31946	1.96504	62775	12630
Heavy hydrocarbs.	C ₂ H ₄	434	41387	0.528173	21848	41387	1.42908	59145	21848
Oxygen.	O ₂	30	2860	0.272962	0.000783	2860	1.250966	3418	0.000783
Carbon monoxide.	CO	996	94980	0.302674	28748	94980	1.250500	0.118500	28748
Hydrogen.	H ₂	0.4524	0.431417	0.304933	0.131550	0.431417	0.089523	38621	131550
Marsh gas.	CH ₄	0.3016	0.287611	0.423924	0.121925	0.287611	0.715006	0.205642	121925
Nitrogen.	N ₂	463	44153	0.305725	13498	44153	1.254400	55369	0.013498
Specific gravity 0.445 compared } Specific heat } 0.342210									
Dry air at 0° C. and P. = 760.0 mm. } @ cubic meter }									
Weight of 1,000 liters of gas. T. = 12.6° C. P. = 758.2 mm. (Kilos.). 0.574037 = 953.61 L. T.°B = 760.0									

ATMOSPHERIC AIR REQUIRED FOR COMBUSTION OF ABOVE.

Names of the Constituents.	Volumes of Ingredients Gases.	Same at Standard Temp. and Pressure.	Specific Heat @ Unit Volume of Constituents.	Specific Heat of Component Volumes.	Volumes of Ingr. at Stand. and Temp. Pressure.	Weight of Ingr. @ Meter Cube.	Weight of Constant Volumes.	Specific Heat by Weight.	Specific Heat of Ingredients by Weight.
Watery vapor.	H ₂ O	0.101207	0.096378	0.345425	0.033292	0.096378	0.804063	0.077494	0.033292
Oxygen.	O ₂	1.160721	1.104773	0.272962	0.301560	1.104773	1.250966	1.382032	0.2182
Nitrogen.	N ₂	4.377000	4.168103	0.305725	1.274294	4.168103	1.254400	5.2268	0.2438

Atmospheric air

5.6383 5.369254

Specific heat of air volume 1.609146

Total specific heat is 1.951356

Can be taken as 1.95 calories @ C°.

Compare this with corresponding quantity in Table VIII.

6.686326

1.609146

We are now in a position to give approximate answers to the queries propounded in the previous pages, and certain others which are always raised in any discussion concerning illuminating gas.

We have already learned that the total "volume of heat," to use a very figurative but expressive method of statement (see page 57), is, using the Bunsen values, 5,880.29 calories if all products are cooled to 0° C. and 5,373.92 calories if the products of combustion escape at 100° C. Under these stated conditions using the Winkler constants the extreme heat production will be 5,840.54 and 5,275.30 calories.

The second question takes a slightly different shape. What is the highest temperature obtainable from the combustion of illuminating gas irrespective of the amount burned, assuming that no heat is lost anywhere, but that all produced is expended simply in producing temperature. To this we will have two pairs of answers, one pair for the Bunsen values and one for the Hempel values.

Bunsen's values. — All products being at last cooled to 0° C.

The temperature will be, per cubic meter of the gas from the mains burned in air: Total heat of combustion in calories divided by the amount of heat required per degree also expressed in calories, or

$$5,880.3 \text{ cal.} / 1.95 \text{ cal.} = 3,015.43^{\circ} \text{ C.}$$

which is the very limit of temperature obtainable by gas and air under ideal conditions. If the products of

combustion are cooled only to 100° C. then the above becomes

$$5,373.92 \text{ cal.} / 1.95 \text{ cal.} + 100^\circ \text{ C.} = 2,855.85^\circ \text{ C.}$$

But such temperatures are not by any possibility to be attained because the conditions assumed are not those of combustion, as within our experience.

The practical limit of heat product and temperature.

—The practical limit of the temperature is not to be determined by any method of analysis, because we have no means of measuring the amount lost, but by means of certain data of not the best possible value the inference has been made that “the loss from conditions not under the control of the experiment is something less than one third, but probably more than one fourth.” Averaging these two statements and assuming that the whole of the balance can be used for raising the temperature of the flame, the resulting quantity becomes

$$\frac{5,373.92 \times 70.83}{1.95 \times 100} + 100 = 2,051.57^\circ \text{ C.,}$$

which is practically identical with the limit which has been reached in certain types of furnace in which the heat loss by way of the outgoing “smoke” is used to heat the incoming gas and air.

It remains to consider the limit of the heat production measured in calories. It must always be remembered that in any machine the useful work is always less than the power expended, and in the flame which is in effect a machine for converting one mode of

motion, chemical action, into another mode of motion, heat, the same fact holds good. We do not, and we can not, cool the products of combustion to zero at the instant, nor at any other time, nor do we cool them to 100°C. , and did we we should defeat our own object, for we would on the instant extinguish the flame. In order that the flame may be self-perpetuating, both the fuel and the sustainer of combustion, both the gas and the air, must be heated to a temperature at which they will take fire spontaneously. That is to say to 600°C. in the case before us. This implies a transfer of heat, motion, from one assemblage or group of atoms to another assemblage or group of atoms or molecules, as we may see fit to consider it, and this can not be done without loss, no matter how small the loss margin may be ; in practice it is not measurable. The heat expended in raising the gas and air to this temperature of spontaneous combustion will be (600×1.95) calories, or 1,170 calories.

This subtracted from the gross heat production $(5,373.92 - 1,170)$ leaves roughly 4,200 calories per meter cube for use in the arts, which may be employed in heating things or for some other useful purpose.

Many persons on all occasions, and nearly every person interested on some occasion, will wish to translate the results obtained from calories per cubic meter to B. T. U. per cubic foot. This is easily done if one has in mind the fact that one calorie is practically equivalent to four British thermal units ($1 \text{ calorie} = 4 \text{ B. T. U.}$) and also that one cubic meter is very nearly

thirty-six cubic feet. Roughly then calories per meter cube divided by nine (cals. @ meter cube/9 = B. T. U. @ cu. ft.) gives the number of B. T. U. per cubic foot. More exactly the relation is $4/35.32 = 0.11325$ \times cals. @ m. cu. = B. T. U. @ cu. ft. In other words 4,200 cals. @ cu. m. = $4,200/9 = 467$ B. T. U. @ cubic foot, or $4,200 \text{ cals.} \times 0.11325 = 472.7$ B. T. U. @ cu. ft.

If we assume the products of combustion to be cooled to steam at 100° C., all other combustion residues being cooled in like manner, the resulting heat production will be not far from 5,200 cals. @ cu. m. or 580 B. T. U. @ cu. ft., how much of this we may use depending on the mechanical perfection of the means employed.

Tension of Aqueous Vapor.*

*Expressed in millimeters of mercury at 0°, density of mercury
13.59593 at latitude 45° and at the sea-level.*

Calculated from Regnault's measurements by Broch (*Trav. et Mém.
du Bur. intern. des Poids et Mes.* 1 A. 33, 1881).

<i>t</i>	Tension	<i>t</i>	Tension	<i>t</i>	Tension		Tension
	mm.		mm.		mm.		mm.
-2.0	3.9499	1.8	5.1975	5.5	6.7357	9.3	8.7224
-1.9	3.9790	1.9	5.2346	5.6	6.7824	9.4	8.7810
-1.8	4.0082	2.0	5.2719	5.7	6.8293	9.5	8.8400
-1.7	4.0376			5.8	6.8765	9.6	8.8993
-1.6	4.0672	2.1	5.3094	5.9	6.9240	9.7	8.9589
-1.5	4.0970	2.2	5.3472	6.0	6.9718	9.8	9.0189
-1.4	4.1271	2.3	5.3852			9.9	9.0792
-1.3	4.1574	2.4	5.4235	6.1	7.0198	10.0	9.1398
-1.2	4.1878	2.5	5.4620	6.2	7.0682		
-1.1	4.2185	2.6	5.5008	6.3	7.1168	10.1	9.2009
		2.7	5.5398	6.4	7.1658	10.2	9.2623
-1.0	4.2493	2.8	5.5790	6.5	7.2150	10.3	9.3241
-0.9	4.2803	2.9	5.6185	6.6	7.2646	10.4	9.3863
-0.8	4.3116	3.0	5.6582	6.7	7.3145	10.5	9.4488
-0.7	4.3430			6.8	7.3647	10.6	9.5117
-0.6	4.3747	3.1	5.6981	6.9	7.4152	10.7	9.5750
-0.5	4.4065	3.2	5.7383	7.0	7.4660	10.8	9.6387
-0.4	4.4385	3.3	5.7788			10.9	9.7027
-0.3	4.4708	3.4	5.8195	7.1	7.5171	11.0	9.7671
-0.2	4.5032	3.5	5.8605	7.2	7.5685		
-0.1	4.5359	3.6	5.9017	7.3	7.6202	11.1	9.8318
		3.7	5.9432	7.4	7.6722	11.2	9.8969
0.0	4.5687	3.8	5.9850	7.5	7.7246	11.3	9.9624
+0.1	4.6017	3.9	6.0270	7.6	7.7772	11.4	10.0283
0.2	4.6350	4.0	6.0693	7.7	7.8302	11.5	10.0946
0.3	4.6685			7.8	7.8834	11.6	10.1614
0.4	4.7022	4.1	6.1118	7.9	7.9370	11.7	10.2285
0.5	4.7361	4.2	6.1546	8.0	7.9909	11.8	10.2960
0.6	4.7703	4.3	6.1977	8.1	8.0452	11.9	10.3639
0.7	4.8047	4.4	6.2410	8.2	8.0998	12.0	10.4322
0.8	4.8393	4.5	6.2846	8.3	8.1547		
0.9	4.8741	4.6	6.3285	8.4	8.2099	12.1	10.5009
1.0	4.9091	4.7	6.3727	8.5	8.2655	12.2	10.5700
		4.8	6.4171	8.6	8.3214	12.3	10.6394
1.1	4.9443	4.9	6.4618	8.7	8.3777	12.4	10.7093
1.2	4.9798	5.0	6.5067	8.8	8.4342	12.5	10.7796
1.3	5.0155			8.9	8.4911	12.6	10.8503
1.4	5.0515	5.1	6.5519	9.0	8.5484	12.7	10.9214
1.5	5.0877	5.2	6.5974			12.8	10.9928
1.6	5.1240	5.3	6.6432	9.1	8.6061	12.9	11.0647
1.7	5.1606	5.4	6.6893	9.2	8.6641	13.0	11.1370

* *Hempel's Gas Analysis*, trans. by Dennis, 1902, p. 480.

Tension of Aqueous Vapor—Continued.

<i>t</i>	Tension	<i>t</i>	Tension	<i>t</i>	Tension	<i>t</i>	Tension
	mm.		mm.		mm.		mm.
13.1	11.2097	17.3	14.6702	21.5	19.0400	25.7	24.5164
13.2	11.2829	17.4	14.7630	21.6	19.1567	25.8	24.6620
13.3	11.3564	17.5	14.8563	21.7	19.2740	25.9	24.8084
13.4	11.4304	17.6	14.9501	21.8	19.3920	26.0	24.9556
13.5	11.5048	17.7	15.0444	21.9	19.5105		
13.6	11.5797	17.8	15.1392	22.0	19.6297	26.1	25.1035
13.7	11.6550	17.9	15.2345			26.2	25.2523
13.8	11.7307	18.0	15.3304	22.1	19.7496	26.3	25.4018
13.9	11.8069			22.2	19.8701	26.4	25.5521
14.0	11.8835	18.1	15.4268	22.3	19.9912	26.5	25.7032
		18.2	15.5237	22.4	20.1130	26.6	25.8551
14.1	11.9605	18.3	15.6212	22.5	20.2355	26.7	26.0077
14.2	12.0380	18.4	15.7192	22.6	20.3586	26.8	26.1612
14.3	12.1159	18.5	15.8178	22.7	20.4824	26.9	26.3155
14.4	12.1943	18.6	15.9169	22.8	20.6068	27.0	26.4705
14.5	12.2731	18.7	16.0166	22.9	20.7319		
14.6	12.3523	18.8	16.1168	23.0	20.8576	27.1	26.6263
14.7	12.4320	18.9	16.2176			27.2	26.7830
14.8	12.5122	19.0	16.3189	23.1	20.9840	27.3	26.9405
14.9	12.5928			23.2	21.1110	27.4	27.0987
15.0	12.6739	19.1	16.4208	23.3	21.2388	27.5	27.2578
		19.2	16.5233	23.4	21.3672	27.6	27.4177
15.1	12.7554	19.3	16.6263	23.5	21.4964	27.7	27.5784
15.2	12.8374	19.4	16.7299	23.6	21.6262	27.8	27.7399
15.3	12.9198	19.5	16.8341	23.7	21.7567	27.9	27.9023
15.4	13.0027	19.6	16.9388	23.8	21.8879	28.0	28.0654
15.5	13.0861	19.7	17.0441	23.9	22.0198		
15.6	13.1700	19.8	17.1499	24.0	22.1524	28.1	28.2294
15.7	13.2543	19.9	17.2563			28.2	28.3942
15.8	13.3392	20.0	17.3632	24.1	22.2857	28.3	28.5599
15.9	13.4245			24.2	22.4196	28.4	28.7265
16.0	13.5103	20.1	17.4707	24.3	22.5543	28.5	28.8939
		20.2	17.5789	24.4	22.6898	28.6	29.0622
16.1	13.5965	20.3	17.6877	24.5	22.8259	28.7	29.2313
16.2	13.6832	20.4	17.7971	24.6	22.9628	28.8	29.4013
16.3	13.7705	20.5	17.9071	24.7	23.1003	28.9	29.5722
16.4	13.8582	20.6	18.0176	24.8	23.2386	29.0	29.7439
16.5	13.9464	20.7	18.1288	24.9	23.3777		
16.6	14.0351	20.8	18.2406	25.0	23.5174	29.1	29.9165
16.7	14.1243	20.9	18.3529			29.2	30.0900
16.8	14.2141	21.0	18.4659	25.1	23.6579	29.3	30.2644
16.9	14.3043			25.2	23.7991	29.4	30.4396
17.0	14.3950	21.1	18.5795	25.3	23.9411	29.5	30.6157
		21.2	18.6937	25.4	24.0838	29.6	30.7928
17.1	14.4862	21.3	18.8085	25.5	24.2272	29.7	30.9707
17.2	14.5779	21.4	18.9240	25.6	24.3714	29.8	31.1494

Tension of Aqueous Vapor.—Continued.

<i>t</i>	Tension	<i>t</i>	Tension	<i>t</i>	Tension	<i>t</i>	Tension
	mm.		mm.	°	mm.	°	mm.
29.9	31.3291	31.0	33.3664	32.1	35.5186	33.1	37.5796
30.0	31.5096	31.1	33.5573	32.2	35.7201	33.2	37.7914
30.1	31.6910	31.2	33.7491	32.3	35.9226	33.3	38.0042
30.2	31.8734	31.3	33.9419	32.4	36.1261	33.4	38.2180
30.3	32.0567	31.4	34.1356	32.5	36.3307	33.5	38.4329
30.4	32.2410	31.5	34.3303	32.6	36.5363	33.6	38.6488
30.5	32.4262	31.6	34.5259	32.7	36.7429	33.7	38.8657
30.6	32.6124	31.7	34.7225	32.8	36.9505	33.8	39.0837
30.7	32.7995	31.8	34.9201	32.9	37.1592	33.9	39.3027
30.8	32.9875	31.9	35.1186	33.0	37.3689	34.0	39.5228
30.9	33.1765	32.0	35.3181				

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